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Suggestions to Authors of the Reports of the United States Geological Survey, 5th ed. Washington, D. C., 1958 (Government Printing Office, $1.75)

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APRIL 1960

HIGH PRESSURE STUDIES OF THE SYSTEM Mg_2GeO_4–Mg_2SiO_4 WITH SPECIAL REFERENCE TO THE OLIVINE-SPINEL TRANSITION*

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ABSTRACT. The system Mg_2GeO_4–Mg_2SiO_4 has been studied to the experimental limits of available hydrothermal and uniaxial high pressure apparatuses.

The inversion temperature for the $Mg_2GeO_{4(spinel)}$–$Mg_2GeO_{4(olivine)}$ equilibrium is 810°C at atmospheric pressure. The ΔV of the inversion is 3.5 cc/mole; ΔH is 3690 ± 180 cal/mole. The inversion temperature is raised by 0.025°C/bar for the first 5500 bars. Infra-red absorption spectra, x-ray intensities and molar refractivities clearly show that Mg_2GeO_4 is an inverse spinel.

Solid solution between Mg_2GeO_4 and Mg_2SiO_4 is complete in the olivine phase at temperatures above that of the inversion in Mg_2GeO_4. The maximum silicate content of the spinel solid solutions at lower temperatures increases steadily with pressure, from 10 mole percent at 700 bars to 50 mole percent at 60,000 bars at 542°C. Extrapolation places the spinel-olivine transition for Mg_2SiO_4 at 100,000 ± 15,000 bars. The change in the lattice spacings of the spinel solid solutions of $Mg_2(Ge,Si)O_4$ shows that $Mg_2SiO_{4(spinel)}$ has a cell edge of 8.22Å. Therefore the ΔV for this transition is 2.0 cc/mole. The pressure dependence of the transition in Mg_2SiO_4 is estimated by extrapolation at 0.013°C/bar.

Experiments show that substitution of Fe^{2+} for Mg^{+2} markedly increases the maximum silicate content of the spinel solid solution under corresponding p-t conditions.

The geophysical implication of these results is that an olivine-spinel transition in the mantle of the earth does appear to be a reasonable explanation of the seismic and density discontinuities starting at 400 km.

INTRODUCTION

In a paper presented to the Royal Astronomical Society Dr. H. Jeffreys (1936) gave evidence of a discontinuity in the properties of the earth some hundreds of kilometers beneath the surface. He reported that at a depth of 480 ± 20 kilometers a change could be measured in the velocities of seismic waves. Specifically P-waves above this depth had a velocity of 9.08 km/sec, but below this depth the velocity was 9.8 km/sec. Calculations by K. E. Bullen (1936) for the density distribution in the earth also suggested a nearly discontinuous change in density at a depth of 300-400 km. Since no known materials could fit this data Dr. J. D. Bernal, in attendance at the meeting, was asked if it was likely that an olivine-like material could be converted to a new state at great pressures. A direct quotation from Observatory (1936) will serve to present important crystal chemical concepts in the paraphrase of Dr. Bernal's discussion:

> Dr. J. D. Bernal said at ordinary pressures olivine, which is magnesium orthosilicate with part of the magnesium replaced by ferrous iron, is a hexagonal lattice of oxygen atoms in which the silicon and metals occupy the cavities, somewhat unsymmetrically. It appeared possible that when the lattice was much compressed the cavities might become too small to hold the silicon atoms, and a different

* Contribution No. 58-117, The Department of Geophysics and Geochemistry, The Pennsylvania State University, University Park, Pennsylvania.

> structure would have to be found. The structure of a crystal was largely a matter of the sizes of the atoms, the cavities having to be neither too large nor too small to hold them. Thus the effect of compressing the lattice as a whole would be similar to that of inserting a larger atom, such as a germanium in place of silicon. Magnesium germanate had been studied by Goldschmidt and found to exist at ordinary pressures in two forms, one isomorphous with olivine and the other cubic. The latter is about 9 percent denser, and therefore is the high pressure form. By analogy it therefore seemed probable that at high pressure olivine would adopt a cubic form. The change of density suggested by the germanate would be of the right order of magnitude.

The reference to V. M. Goldschmidt introduces a series of developments having to do with the reality of the transition noted by Goldschmidt (1931). In a footnote in this paper it was stated that magnesium orthogermanate, Mg_2GeO_4, was prepared in a spinel-like form. A year later Jander and Stamm (1932) placed the inversion temperature for the spinel-olivine polymorphs at 1063°C. Incidental to work on synthetic clay phases, Roy and Roy (1954) prepared reproducibly under high water pressures the Mg_2GeO_4 as euhedral spinel-structure crystals. Aware of the change in density of the polymorphs as reported by Bernal and restated by B. Mason (1952), Roy and Roy determined fairly accurately the volume change as 8.3 percent of the spinel volume. They gave the inversion temperature as 1005°C using dry techniques. This work has in general been overlooked since it appeared with much other material on a different subject. Subsequent to this time four reports appeared with the claim that the spinel polymorph of Mg_2GeO_4 *could not be made*. Thus Urey (1952) says

> . . . the observations of Goldschmidt were very approximate and it has proven impossible to prepare the cubic modification in this laboratory. Therefore, Bernal's suggestion rests only on pure hypothesis and it seems desirable to explore the possibility that iron phase is present in the mantle.

Similarly Ringwood (1956) says

> The evidence . . . indicates that the olivine structure is probably thermodynamically stable above 600°C. Accordingly the author would agree with Romeijn that Jander and Stamm were probably wrong about the transition of Mg_2GeO_4 at 1065°C.

It is of interest to note that although Romeijn (1953) had to conclude that the dimorphism did not exist, he did acknowledge that the absence of dimorphism in Mg_2GeO_4 was a serious flaw in his analysis of spinel structures. E. F. Bertaut in his early work with germanate spinels (1954 and personal communications) was likewise unable to make the spinel form.

The location with respect to depth of the seismic discontinuity reported by Jeffreys has also been changed with subsequent investigations. The current belief is that two discontinuities exist, one at 413 km and one at 984 km. Mason (1952) summarizes the general implications of the hypothesis of solid phase changes in this manner:

> . . . olivine would begin to change to a higher-density polymorph at a depth of 413 km, and the change would become complete at a depth of 984 km. The change would be gradual through the intervening region, the transition depending on temperature, pressure and the magnesium-iron ratio in the olivine, all of which probably vary with depth. A polymorph change of this sort within the mantle also provides a mechanism for periodic orogeny; an increase in the amount of the denser polymorph during geological time would result in contraction of the earth as a whole, thus giving a plausible explanation for crustal shortening and orogeny. All this is highly speculative, however. As Adams (1947) remarked, speculation of this kind point up the desirability of devising means for the investigation of

phase changes in silicates at pressures of the order of 10^6 atm and temperatures above 1,000°.

Obviously a direct experimental attack on the problem of a transition in natural olivine was not possible with known and available techniques and apparatus. However, it was decided that a fruitful and feasible approach to the problem would be a study of the system Mg_2GeO_4-Mg_2SiO_4, with emphasis on solid solubility and on the polymorphic transitions of the olivine to the spinel type with a view to obtaining reliable data on the Mg_2SiO_4 by extrapolation. The essence of the experimental approach and some results, including the effect of the substitution of some Fe^{2+} for Mg^{2+} were reported to the Geological Society of America, Minneapolis meeting (1956). Additional work concerned with some modification and calibration of high pressure apparatus was reported to the same group at the Atlantic City meeting (1957), and at the St. Louis meeting (1958) the results of work on the system Mg_2GeO_4–Mg_2SiO_4 at pressures up to 60 kilobars were presented.

EXPERIMENTAL PROCEDURES

Work was begun on the system Mg_2GeO_4–Mg_2SiO_4 using the hydrothermal techniques necessary to catalyze reaction in the solid state. Details of the basic apparatus for these techniques are given by Roy and Tuttle (1956) and Roy and Osborn (1952). The hydrothermal bombs may be used to provide desired and controlled pressure and temperature conditions on prepared samples. The practical upper limits of pressure are 60,000-70,000 psi and of temperature 900-1,000°C, but these limits are not coincident. The higher pressures lower considerably the usable temperature limits.

A second major piece of apparatus necessary in the investigations is the uniaxial pressure device in which pressures can be attained an order of magnitude greater than those feasible in the test tube bomb apparatus. Generally the unit is a modification by Tuttle and Harker in our laboratory on designs of Bridgman along the lines of Griggs and Kennedy (1956).

A description of equipment and procedures is given elsewhere (Dachille and Roy, in press a). In this type of device a large thrust is developed by a hydraulic ram which is intensified and transmitted into a small sample by the use of very hard small piston faces. These pistons have been made of cemented carbides, polycrystalline alumina or mullite, or of special hardenable steels. Directed pressure, that is, total thrust divided by reduced area, may approach 900,000 to 1,000,000 psi, but the effective coincident temperature limits fall very rapidly to about 600°C at these pressures. Pressure to the "jack" is supplied and automatically controlled by means of a Foxboro controller and Aminco oil pump. Temperatures are controlled by Honeywell millivoltmeter instruments. Many techniques for experiments at these pressures were worked out during this and allied studies with a view to studying reversible equilibria rather than only preparing phases. Thus in general we have made efforts to make runs from 1 day to 2 weeks long rather than several minutes to a few hours. It is perhaps accurate to say that no similar work has been described either with respect to range or detail other than that of MacDonald (1956).

The petrographic microscope and the x-ray diffractometer were the primary analytical tools, the latter being much more useful to give not only the

phases present but their composition from the spacings. A Perkin-Elmer Double Beam Model 21 infra red spectrometer was used to obtain absorption spectra in series of compounds with systematic substitution of one cation for another to indicate the coordination of the ion in the spinel phases.

PREPARATION OF MIXTURES

The method of preparation of most of the mixtures in this study was the direct mulling of the finely powdered oxides under absolute alcohol, then heating for 2-3 hours at 400°C. The magnesia was C. P. Reagent grade of Baker and the germania was the soluble form of GeO_2 prepared by the Eagle-Picher Company. Silicon dioxide was used in the form of silicic acid, the water content of which was determined by dehydration at 1350-1400°C.

A few mixtures used were prepared by the nitrate method and by the method of coprecipitation of germanium and silicon hydrous gels from solutions of their tetrachlorides (Roy, 1956). No significant advantages were found with these latter methods so that systematic work was restricted to mixtures prepared from the oxides.

TABLE 1

X-ray data on Mg_2GeO_4 and Mg_2SiO_4 spinel and olivine polymorphs

	SPINEL				OLIVINE			
	Mg_2GeO_4		Mg_2SiO_4		Mg_2GeO_4		Mg_2SiO_4**	
hkl	d(A)	I(est.)	d(A) (extrap.)	hkl	d(A)	I(est.)	*	
111	4.77	40	4.74	020	5.15	20	5.11	26
220	2.92	30	2.907	110	4.44	40		
311	2.492	100	2.480	021	3.91	80	3.88	69
222	2.384	2	2.374	101	3.81	10	3.73	25
320	2.292	2	2.280	111,120	3.57	10	3.487	21
400	2.066	10	2.056	121	3.06	10	3.000	17
330	1.947	5	1.938	130	2.619	20	2.768	53
331	1.896	10	1.886	131	2.546	100	2.513	73
422	1.687	50	1.678	112	2.488	90	2.458	100
333	1.590	50	1.583	041	2.364	10	2.348	9
	*		***	210	2.390		2.316	9
	a = 8.255A		8.22A	122	2.295	10	2.268	59
	b = "			140	2.279	2	2.250	33
	c = "			211	2.220	20	2.161	15
	v = 562.5A³		555.4	132	2.056	2	2.034	5
	z = 8		8	042	1.956	2	1.945	4
				150	1.898	2	1.878	5
				113	1.825		1.811	2
				151	1.810		1.792	3
				222	1.783	20	1.748	60
				241	1.730	2	1.670	13
				061	1.652	5	1.636	12
				133	1.632	5	1.618	15
				152	1.603	5	1.589	2
				043	1.581	10	1.572	10
					4.915A		4.76A	
					10.295		10.20	
					6.020		5.99	
					304.6(609.2)		290.8(581.6)	
					4(8)		4(8)	

* Roy and Roy (1954)
** Swanson and Tatge NBS Circular 539, v. 1
*** Extrapolated from figure 2.

In the course of the investigation starting compounds were prepared by the hydrothermal treatment or even dry fusion of the oxide mixtures. Compounds so prepared were then used to test a criterion of reversibility in transitions or to seek clear evidence of exsolution and change in solid solubility under various conditions of pressure and temperatures.

RESULTS

Data on the phases encountered.—In table 1 are recorded the characteristic x-ray diffraction data for the olivine and spinel polymorphs of Mg_2GeO_4. Data for the olivine phase of Mg_2SiO_4, forsterite, are included to permit a direct comparison with the germanate isomorph. Further x-ray data are given in figures 1 and 2 to demonstrate the effect of replacing some of the ger-

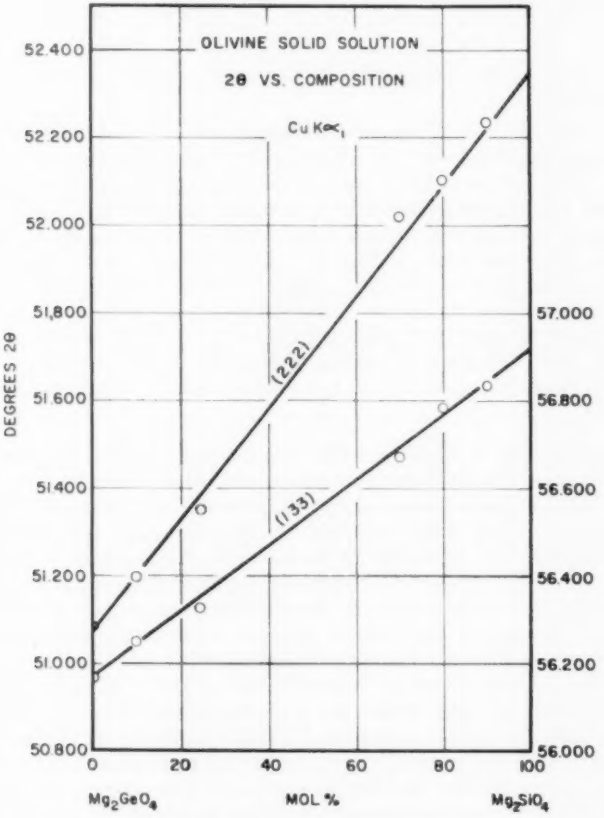

Fig. 1. System Mg_2GeO_4-Mg_2SiO_4. Change of 2θ values with composition of the olivine polymorph.

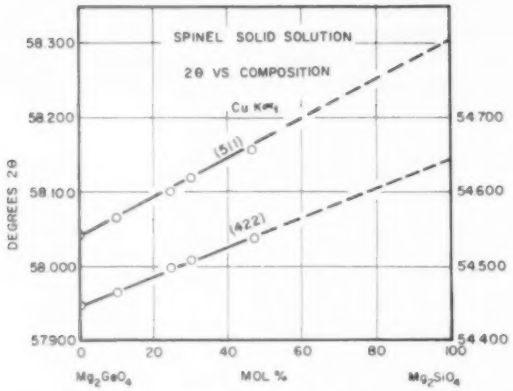

Fig. 2. System Mg_2GeO_4-Mg_2SiO_4. Change of 2θ values with composition of the spinel polymorph.

manium with silicon in the olivine and spinel phases respectively. The shifts in these "d-spacings" approach the ideal Vegard relation for substitution in solid solution. They will permit a comparison of volume change between the olivine and spinel polymorphs up to almost 50 percent silicate content, the upper limit of the spinel solid solution prepared. Extrapolation of the d-spacings, figure 2, show that the spinel phase of Mg_2SiO_4 will have a cell edge of 8.22 A and a unit cell volume of 555.4 A^3. This volume is only 4.7 percent smaller than that of the olivine. Hence the volume change in the silicate end number is only 56 percent of that found in the germanate. Although such an extrapolation is considerably more reliable than various guesses in the past, the possibility of strong deviations from ideality in spinel solid solutions cannot be completely ignored.

The transition in Mg_2GeO_4.—The end member Mg_2GeO_4 provided an example for a direct study of the pressure-temperature dependency of the olivine-spinel inversion within limits set by the hydrothermal apparatus. Clean cut and easy reversibility of the transition was achieved under hydrothermal conditions (see table 2). At 10,000 psi the transition occurs at 823°C and the use of higher pressures raises the temperature rapidly to the point at which bomb damage or failure occur frequently. Nevertheless a number of runs were made at higher temperatures and pressures in order to follow this dependence. Similarly equipment problems limited the exploration by the uniaxial devices. It was possible however to make a number of runs at pressures and temperatures approaching 1,000°C and 100,000 psi in this equipment by using pistons made of polycrystalline Al_2O_3 or of mullite. Within these limits the pistons held up remarkably well with no distortion of the circular faces bearing the maximum stress. Unfortunately these surfaces were subject to pitting or flaking when they were separated to recover the sample wafer so that regrinding of the pistons was necessary after each run. Further, the pistons, which were made of rods 4 inches by 1 inch in diameter, on continued use did fail by shearing and

splitting at pressures considerably below 100,000 psi. The information from these experiments is collected in table 2 and the pressure-temperature dependency deduced therefrom is indicated in figure 3. From the slope of this line and the measured difference in volume of the two polymorphs at some selected temperature, it is possible to calculate from the Clapeyron equation a change in enthalpy for the transition. The ΔH of transition obtained (olivine-spinel) is 19.9 cal/gm or 3,690 cal/mole with an error of $\pm$ 5 percent. These values will be reviewed later in the discussion.

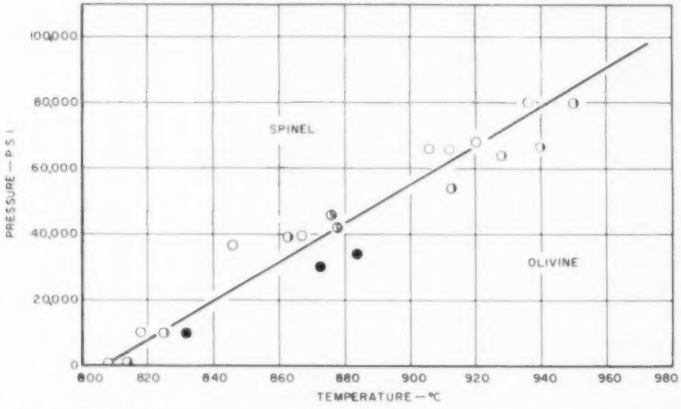

Fig. 3. Univariant p-t curve for the spinel-olivine transition in Mg_2GeO_4. (Partially filled circles indicate persistence or formation of olivine. Curly division shows runs in which pistons fractured after start of spinel phase.)

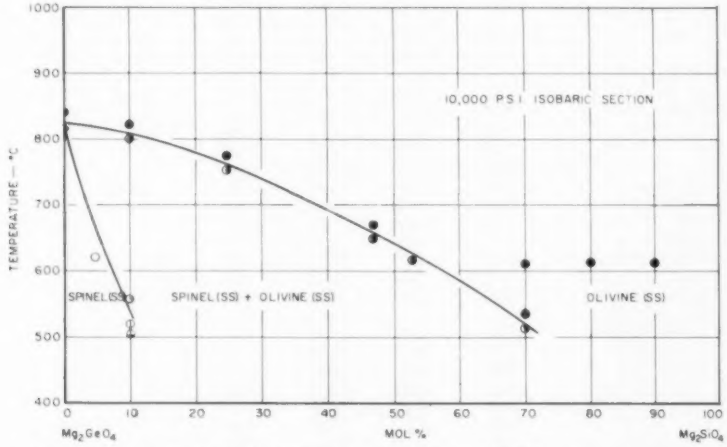

Fig. 4. System Mg_2GeO_4-Mg_2SiO_4—Isobaric section at 10,000 psi water pressure.

TABLE 2

Data on the system Mg_2GeO_4–Mg_2SiO_4

Composition	Run (No.)	(°C) Temp.	Pressure 1000 psi	Duration Hrs.	Phase
Mg_2GeO_4 (Hydrothermal) Oxides	7043	925	5	15	Olivine
"	7153	833	10	70	"
"	7076	830	10	70	Spinel & ol.
"	7081	828	10	70	Sp. + trace ol.
"	7088	822	10	120	Sp.
"	7089	801	1	200	Sp.
"	7094	808	1	44	Sp.
"	7096	813	1	90	Sp. + trace ol.
"	7107	830	26	70	Sp.
"	7146	873	30	40	Ol.
"	7148	864	39	40	Sp. + trace ol.
Spinel Form	7135	865	39	40	Sp.
Olivine Form	7136	865	39	40	Sp. + minor ol.
Spinel Form	7028	820	10	20	Sp.
" "	7029	825	10	40	Sp. + trace ol.
" "	7030	845	10	44	Sp. + minor ol.
" "	7031	875	10	40	Ol.
" "	7133	845	37	40	Sp.
Olivine Form	7134	845	37	40	Sp. + trace ol.
(Uniaxial) Oxides	7437	925	150	1	Split. Spinel, MgO, GeO_2 ru.
"	7441	1088	90	½	Split. trace ol. MgO, GeO_2
"	7444	906	69	6	Dry. MgO, GeO_2 ru.
"	7445	903	73	24	Sp. + trace GeO_2, MgO
"	7451	913	57	24	Sp. + ol.
"	7454	938	65	40	Trace sp. + ol. + oxides
Spinel Form	7457	958	78	40	Sp. + ol. trace
" "	7458	950	36	2	Split. + ol. tr.
" "	7460	918	72	60	Sp.
" "	7485	925	62	40	Sp. + tr. ol.
" "	7479	935	62	40	" + " "
Olivine Form	7489	930	62	40	Spinel
" "	7500	868	32	40	Olivine
" "	7501	863	32	40	"
Oxides + olivine seeds	7524	927	61	40	Sp. + tr. ol.
" " " "	7529	934	52	60	" + ol.
" " " "	7532	910	50	40	" + tr. ol.
(Hydrothermal) 5 mol% Mg_2SiO_4	7016	548	10	47	Sp. + tr. ol.
" "	7121	623	10	80	"
" "	7108	626	10	40	"
" "	7095	640	10	96	"
" "	7021	670	10	48	" + " "
" "	7056	745	10	200	" + minor ol.
" "	7078	812	10	96	Ol. + tr. sp.

TABLE 2 (Continued)

Composition	Run (No.)	(°C) Temp.	Pressure 1000 psi	Duration Hrs.	Phase
10% "	7091	521	10	80	Sp. + serp.
" "	7583	529	10	72	" + tr. serp.
" "	7017	548	10	47	" + " ol.
" "	7087	595	10	70	" + minor ol.
" "	7079	814	10	96	Ol.
" "	7063	821	10	72	"
24.8% "	7018	548	10	47	Sp. + ol.
" "	7057	750	10	240	"
" "	7064	772	10	70	Ol.
30% "	7164	665	10	90	"
" "	7073	712	10	48	" + minor sp.
47% "	7053	650	10	30	" + tr. sp.
" "	7003	651	10	48	" + " "
" "	7023	670	10	48	" + " "
53% "	7554	613	10	70	" + " "
70% "	7161	503	10	120	" + " talc.
" "	7583	529	10	72	" + " sp. & talc.
5 mol% Mg_2SiO_4	7109	626	55	48	Sp.
10 "	7105	565	55	40	"
10 "	7104	584	54	72	" + tr. ol.
24.7 "	7155	745	67	10	" + minor ol.
24.7 "	7157	796	52	29	Ol. + minor sp.
30 "	7156	745	67	10	" + " "
30 "	7158	796	52	29	"
47 "	7162	737	54	48	"
47 "	7160	770	54	9	"
70 "	7183	652	45	24	"
70 " (Uniaxial)	7184	595	53	72	"
Oxides					
10 mol% Mg_2SiO_4	7548	543	122	70	"
18 "	7573	540	282	21	"
18 "	7570	547	196	14	" + tr. ol.
18 "	7568	605	200	24	" + " "
24.7 "	7546	542	260	44	" + " "
24.7 "	7530	542	450	48	" + " serp.
24.7 "	7520	570	570	46	"
24.7 "	7541	546	203	25	" + minor ol.
24.7 "	7476	560	350	24	" + " " (3/8" sample)
30 "	7563	537	515	23	" + tr. ol.
30 "	7569	545	553	16	" + " "
30 "	7537	547	405	48	" + " "
38 "	7571	537	740	12	"
38 "	7559	538	570	22	" + minor (GeO_2 rut.)
47 "	7562	530	750	11	" + tr. (GeO_2 rut)
47 "	7567	530	849	6	" + tr. " tr. talc.
47 "	7527	541	585	48	" + minor ol.
47 "	7468	545	670	22	" + " "
47 "	7561	622	190	22	" + " "
53 "	5797	542	780	5	" + " "
53 "	7534	562	408	32	" + 20% "
70 "	7596	536	950	3½	" + ol. (3/8" s.)
80 "	7579	530	200	24	No H_2O. No reaction
80 "	7555	538	100	23	Ol.
80 "	7550	540	311	20	" + minor serp.

The system Mg_2GeO_4–Mg_2SiO_4.—Data from critical runs in the hydrothermal and uniaxial pressure units are collected in table 2. From these data the phase diagrams shown in figures 4, 5, 6, and 7 have been constructed. The dashed portions in these figures indicate regions not accessible to the known and available techniques. However, the two rather complete isobars at 10,000 and 55,000 psi and the isotherm at 542° (fig. 8) indicate a self consistency in the pressure-temperature-composition relations of the system. Figure 9 is a three dimensional p-t-x diagram of the system Mg_2GeO_4–Mg_2SiO_4 constructed from the data.

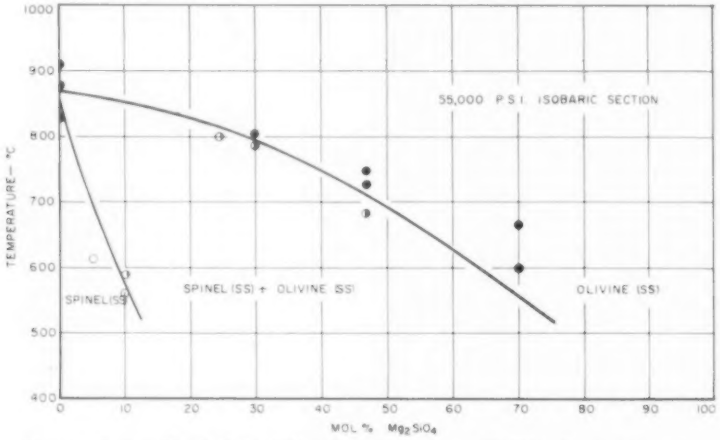

Fig. 5. System Mg_2GeO_4-Mg_2SiO_4—Isobaric section at 55,000 psi water pressure.

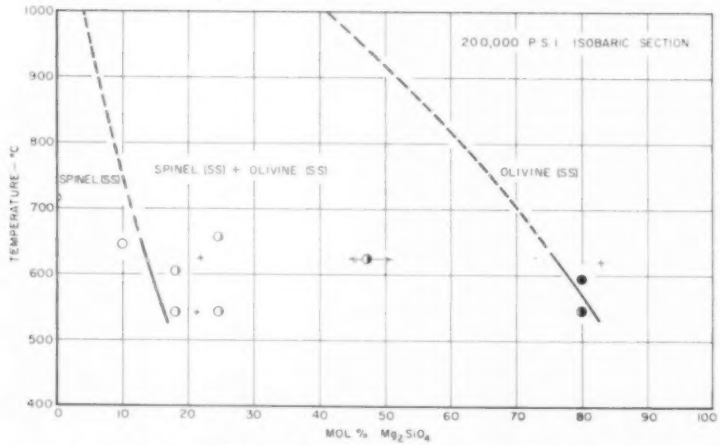

Fig. 6. System Mg_2GeO_4-Mg_2SiO_4—Isobaric section at 200,000 psi (uniaxial pressure).

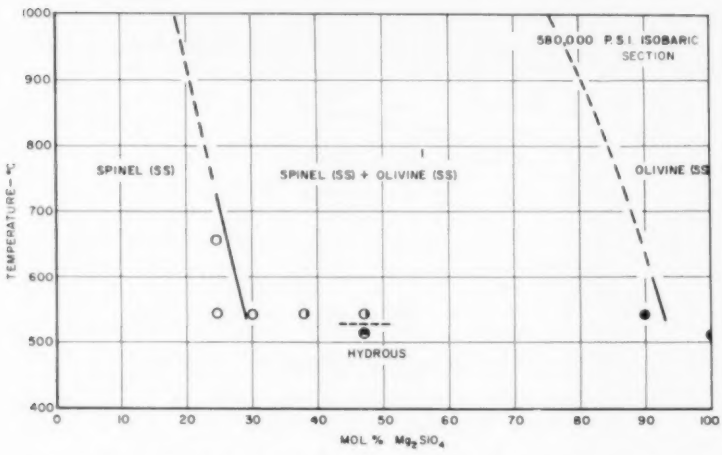

Fig. 7. System Mg_2GeO_4-Mg_2SiO_4—Isobaric section at 580,000 psi (uniaxial pressure).

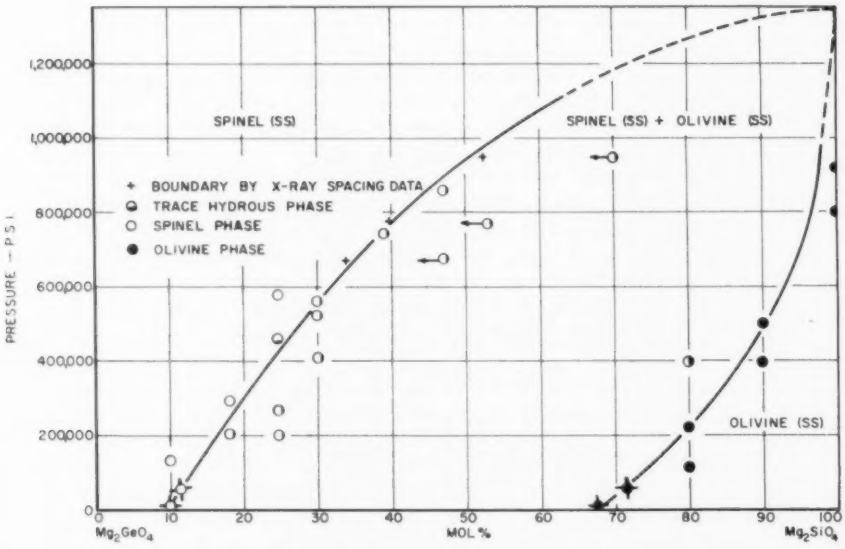

Fig. 8. System Mg_2GeO_4-Mg_2SiO_4—Isothermal section at 542°C (uniaxial pressure).

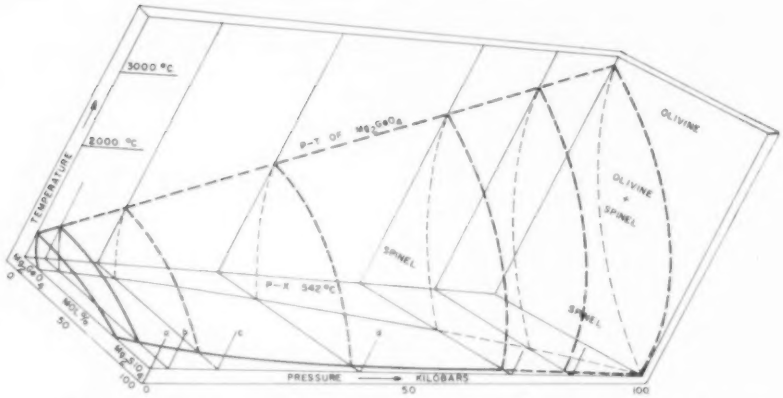

Fig. 9. Perspective of p-t-x of system Mg_2GeO_4-Mg_2SiO_4. Sections a, b, c, and d are isobars of preceding figures. The isotherm of figure 8 provides base of the construction.

Substitution of Fe^{2+} for Mg^{2+}.—The term olivine has the very definite connotation in mineralogy of an iron bearing magnesium orthosilicate. In fact, the word is applied as a group name for the solid solution series between forsterite, Mg_2SiO_4 and fayalite, Fe_2SiO_4. The importance of Fe^{2+} as an additional component in the system under study was recognized early in the experimental work. A number of runs were made with starting mixtures in which a portion of the Mg^{2+} was replaced by Fe^{2+}. Fayalite compositions also were used in seeking a direct inversion of fayalite to a spinel-like form. The problem of maintaining the oxidation state of Fe^{2+} was tackled by the use of ferrous oxalate in the starting mixture, and the addition of powdered metallic iron. In the uniaxial pressure device the samples in some runs were encased in pure iron rings and disks. Data for this phase of the investigation are in table 3. Reaction products were often rather difficult to identify unambiguously so that working out phase boundaries in detail by phase identification would be a tedious job even in a study directed specifically at this system. However, the data do show plainly that in any isobaric section the spinel solid solution area is appreciably larger than that in the completely magnesian system. Increasing the Fe^{2+} content broadens further the spinel solid solution field so that one might expect the fayalite inversion pressure to be relatively low. The poor spinel-like x-ray pattern obtained on a fayalite composition at about 500,000 psi may very well be a confirmation of this observation.[1] However, this could well be a solid solution between Fe_2SiO_4 and Fe_3O_4. Quantitative work in this field was postponed in view of the elaborate arrangements which would be necessary to control the valence of the iron. Indeed it is not even sure whether Fe^{2+} and Ge^{4+} could exist in equilibrium (Muan, personal communication) although Bertaut claims to have made Fe_2GeO_4. Routine chemical analysis of

[1] A. E. Ringwood subsequently appears to have confirmed this finding in his brief note (1958a) on the formation of a spinel form of Fe_2SiO_4 at 400°C and 45 kilobars. A more complete description of his results in this area appeared recently (1958b).

TABLE 3

Data for the system Mg_2GeO_4–Mg_2SiO_4 with Fe substitution for Mg

Composition Mg/Fe	Ge/Si	Run No.	(°C) Temperature	1000 psi Pressure	Duration (hrs.)	Phases
9:1	7:3	7169	715	10	60	Ol. + Sp. + ?
9:1	7:3	7170	737	10	60	Added Fe. Less sp.
"	10:0	7171	699	10	80	Sp. complete Sp.
"	7:3	7172	813	10	40	Added Fe. Ol., sp.
"	"	7173	915	10	20	Olivine
"	"	7174	544	10	60	Olivine, Serp.
"	"	7175	880	10	40	Trace sp.
"	"	7176	880	10	40	Added Fe. Ol.
9:1	1:1	7177	704	10	40	" " sp.
9:1	1:1	7179	745	10	40	Excess Fe. Sp.
9:1	7:3	7181	650	180	190	Oxides + trace sp.
9:1	85:15	7182	720	10	20	Sp. + ol.
9:1	85:15	7185	633	10	90	All spinel
9:1	7:3	7186	628	170	160	Sp. + tr. ol. Hematite, serp.
8:2	7:3	7187	655	11	70	Sp. + minor ol.
8:2	7:3	7188	592	11	70	Sp. + trace ol.
8:2	7:3	7189	740	11	70	Sp. + ol.
8:2	7:3	7190	600	180	190	" hematite
8:2	7:3	7225	530	250	70	" "
8:2	7:3	7229	520	350	90	" carbonates
9:1	1:1	7230	540	350	90	No reaction
Natural Olivine		7236	515	250	250	Ol. + serp. + enstatite
$2FeO.SiO_2$		7249	542	180	70	Oxides
"		7391	550	720	40	Cubic phase, green

these very small samples was not attempted in view of the problem of the added iron or contamination from the iron washers.

DISCUSSION

Effect of water.—All through the investigation water was used, and considered, strictly as a catalytic agent. In a few runs, however, it did enter into the composition of the products with the formation of small amounts of germanium-bearing serpentines and talcs together with either the olivine or the spinel phases. Since the main interest was in the phase relations of the olivine-spinel polymorphs conditions leading to the production of hydrous phases were avoided whenever possible. Hydrous phases appeared at temperatures below 520-523° in the lower pressure studies, but also appeared at temperatures close to 542° at the higher pressures. The latter appearances are somewhat suspect because of the possibility of the hydrous phases forming while quenching the runs, but they cannot be dismissed without further systematic study. It is interesting to note that the stability of the serpentine appears to be affected so little by pressure changes from Roy and Roy's value of 520°C at 1,000 atmospheres to nearly 60,000 atmospheres in this work. Evaluation of the catalytic effect of water in this system can be only qualitative because experiments were not set up to study rate phenomena. It has been pointed out that the Mg_2GeO_4 spinel–olivine reaction was found to take place only above 1,005°C in a dry

system by Roy and Roy (1954). Extrapolating the hydrothermally determined pressure-temperature dependency of the transition back to atmospheric pressure the present data would place the transition near 810°C.

An empirical observation may be made concerning a measure of the "catalytic effect" of water in this reaction. The presence of water enables it to proceed at a rate so that essentially complete conversion may be achieved at a temperature at least 200°C below the equivalent temperature in the absence of water. In this reaction the lower limit is set by the stable equilibrium temperature. In other cases such as the exsolution of Al_2O_3 from spinel solid solutions this catalytic effect in terms of temperature would be 400-500°C. An evaluation of the importance of water-catalysis in terms of time is gained from the following: A reaction of the dry oxides plus water will yield the spinel and forsterite phases in a matter of a few hours in the uniaxial devices. In the total absence of water, two weeks reaction time at 500,000 psi and 450°C failed to react the oxides, although the GeO_2 did go to the rutile form. Numerous observations of this type were made on many reactions in the uniaxial devices which did not go to completion because of loss of added water due to splitting of the reaction capsule or to cracking of the piston surfaces. Thus it was observed that even at 880°C and 45,000 psi reaction which apparently had started the spinel phase growth of Mg_2GeO_4 was interrupted after a few minutes by the cracking of a piston face with the presumable loss of water. The pressure and the high temperature were maintained on the sample at least 10 hours without obtaining complete reaction.

THE NATURE OF PRESSURE IN UNIAXIAL DEVICES

Many observations in this and related studies give support to the interpretation that the pressures calculated, or at least their effects, are very close to those of hydrostatic systems. Considerable work was done expressly to evaluate the nature of the pressure (Dachille, Shafer, Roy, in preparation) but only an outline is given here:

1. Field boundaries in the system Mg_2GeO_4–Mg_2SiO_4 as determined in a purely hydrostatic run, kindly made for us by Dr. H. S. Yoder, at 550° ± 5°C and 10,000 ± 50 bars water pressure agree with those determined in the uniaxial devices.

2. The formation of the CS_2 "polymer" within 10 percent of the 42,000 bars reported by Bridgman (1941).

3. Uniformity of pressure and reproducibility were studied in the SiO_2 quartz-coesite reaction by varying the sample area-metal area ratios and by determining the p-t dependence of this reaction in the 350-650° interval. This dependence was found to be essentially the same as that reported by MacDonald who worked with a sample system entirely omitting a containing ring.

The transitions in Mg_2GeO_4 and Mg_2SiO_4.—The reality and reversibility of the olivine-spinel transition (contrary to the assertion of Bertaut, 1954, 1956) has been amply demonstrated and the equilibrium temperature at atmospheric pressure set at 810°C. In figure 3 the pressure-temperature dependence

of the transition in Mg_2GeO_4 is shown, obtained as a composite of runs from both the hydrothermal and uniaxial pressure systems. The slope of this line is equivalent to the reciprocal of 24.6°C per kilobar with an uncertainty of 1.2°C per kilobar. A precise calculation of the ΔH of transition by use of the Clapeyron equation requires thermal expansion (and compressibility) data of both polymorphs at the inversion. The data are not available and therefore the ΔH has been calculated with the assumption that the volume difference at room temperature applies for the transition at one atmosphere and 810°C. The error in the value caused by neglecting the $\Delta\alpha$ term is unlikely to be more than 1 percent of the total ΔV term since thermal expansion coefficients of similar materials are about 100×10^{-7}/°C. By far the largest error is involved in the graphical determination of the slope.

The pressure-temperature dependence in the transition of the silicate end member is of geological interest but remains beyond direct experimental determination at present. An estimate may be made considering some aspects of the system Mg_2GeO_4–Mg_2SiO_4. In various oversimplified calculations the slope may be assumed to be the same as that of the germanate end member. Therefore in the Clapeyron equation $dt/dp = T\Delta V/\Delta H$ an identity of dt/dp for the germanate and silicate end members requires that the $\Delta V/\Delta H$ ratios are the same for the same absolute temperature. However, the isotherm of figure 8 and the p-t-x of figure 9 suggest that at the pressures at which the transition in the silicate first appears possible the temperature is more than 2,000°C below that of the germanate member. If this difference were only 1,000°C the absolute temperatures of the transitions at 100 kilobars will be nearly 800°K and 1800°K for the silicate and germanate members respectively. The value of dt/dp for the silicate will be correspondingly higher unless the $\Delta V/\Delta H$ value increases in the proportion of 1800/800. The ΔV of the silicate transition is only 56 percent of that found in the germanate. Therefore its ΔH value would have to be only about 25 percent that of the former, illustrating the danger of making simple assumptions. This is in agreement with the work of Majumdar and Roy (1958) which shows there are no data to justify assuming equality or any simple relation between ΔH, ΔV, or dp/dt even for analogous transitions between dimorphic substances, removing any justification that values from the Clapeyron equation can be extrapolated from one isotype to another. The observation by Mason (1952) that the unit cell of spinel Al_2MgO_4 was about 9 percent smaller than the corresponding Mg_2SiO_4 olivine unit encouraged the above assumptions, but it appears that in addition to the above objection an interesting detail of crystal structure intervenes. Later in the discussion it will be shown that the germanate spinel is of the inverse type with Ge^{4+} in octahedral sites whereas in the silicate spinel Si^{4+} is probably in tetrahedral sites. However, in both olivine structures the 4^+ cations are in tetrahedral sites. Therefore, it is reasonable to expect that Ge^{4+} changing from 4 to 6 coordination will produce a greater volume decrease than found in the silicate member where the coordination is unchanged.[2]

[2] The smaller unit cell of the Al_2MgO_4 may mean that in this spinel the Al^{3+} is in fact in octahedral sites in agreement with neutron diffraction confirmation that Al_2MgO_4 is a normal spinel.

In view of the serious limitations of extrapolation of the Clapeyron relations an evaluation of dt/dp of the silicate transition directly by graphical means may be more accurate. Isotherms at 600, 660 and 730°C for the spinel-spinel + olivine boundary from the data and construction of the four isobaric sections are plotted on figure 10 on a logarithmic scale. The isotherm at 542°

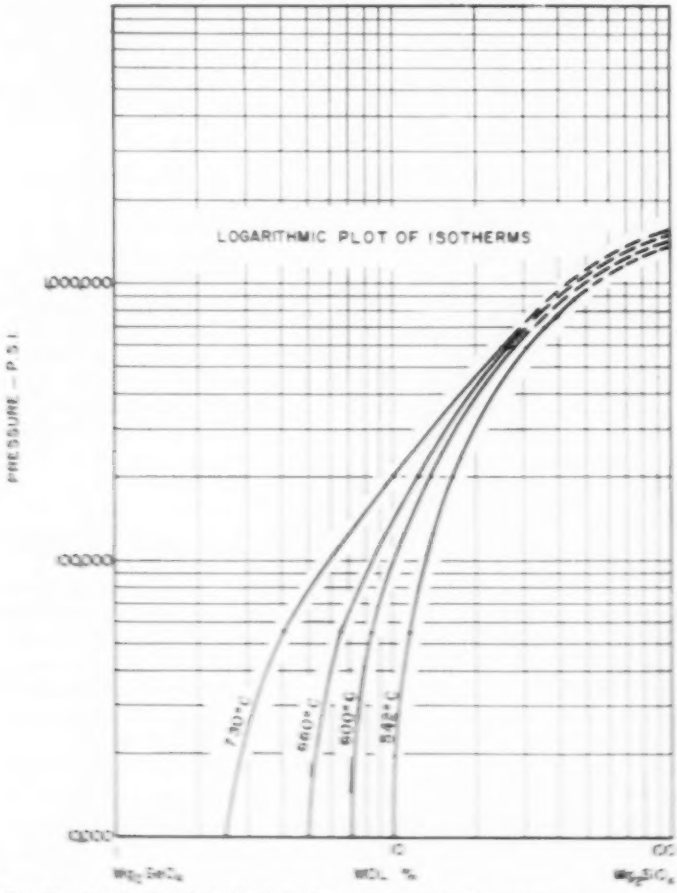

Fig. 10. System Mg_2GeO_4-Mg_2SiO_4. Logarithmic plot of isotherms constructed from data of the t-x and p-x sections.

for the same boundary also is plotted to include the results at higher experimental pressures. From the results of graphical extrapolations to 100 percent the values of dt/dp obtained are seen to decrease from 24.6°C per kilobar for the germanate member to about 23°C per kilobar for the silicate member.

The experimental work on the substitution of some Fe^{2+} in the system does no more than indicate that the spinel phase is stable to higher temperatures (or lower pressures) than in the iron free systems. The effect of fayalite solid solution on dt/dp cannot be determined from our data, but for substitutions up to 20 mol percent an assumption is made that it is the same as that of the magnesian member. From these data and the few runs on the Fe_2SiO_4 composition one can only confirm that which is easily guessed that the presence of Fe^{2+} in the olivine will lower the pressure necessary for its transition to a spinel.

Certain geophysical implications of the data.—A consideration of the geophysical aspects of the results is summarized in figure 11. On this figure are

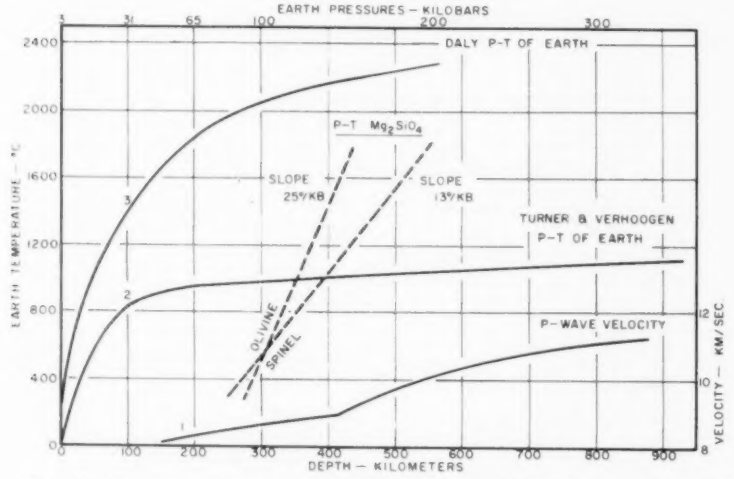

Fig. 11. Pressure, temperature and p-wave velocity relations for a portion of the mantle on which are superimposed possible p-t relations of Mg_2SiO_4.

shown for a portion of the earth 1) the variation of the P-wave velocity 2) the pressure-temperature relation of Turner and Verhoogen (1951) 3) the pressure-temperature relation of Daly (1943). The two p-t lines representing the limits of the uncertainty of the p-t dependence of the Mg_2SiO_4 transition, have slopes of nearly 25 and 13°C per kilobar and are plotted passing through 542° and 100 kilobars (300 kilometers depth).

An inspection of figure 11 shows that a transition of olivine to spinel could be the determining factor in the second order discontinuity just below 400 km depth. If the seismic discontinuity is accurately placed at 413 km depth and if the composition of the mantle is essentially forsterite with up to 10-20 mol percent fayalite, the main considerations then are the dt/dp of the transition and the p-t curve of the earth.

It is clear that using either of the widely divergent earth p-t curves, one can reconcile the seismic discontinuity "reasonably" with the transition. The

general agreement is certainly in the right order of magnitude since the experiments conclusively rule out 10 or 1,000 kilobars as the transition pressure at say 1,000°C. The problem to determine directly the p-t relation of the transition for forsterite in order to narrow the uncertainty of the extrapolation made here remains urgent. These refinements will then permit a closer examination of the temperature variation in the earth.

CRYSTAL CHEMICAL OBSERVATIONS

In work from this laboratory (Dachille and Roy, 1959) it has been shown that in the absence of the complete assignment of absorption frequencies in

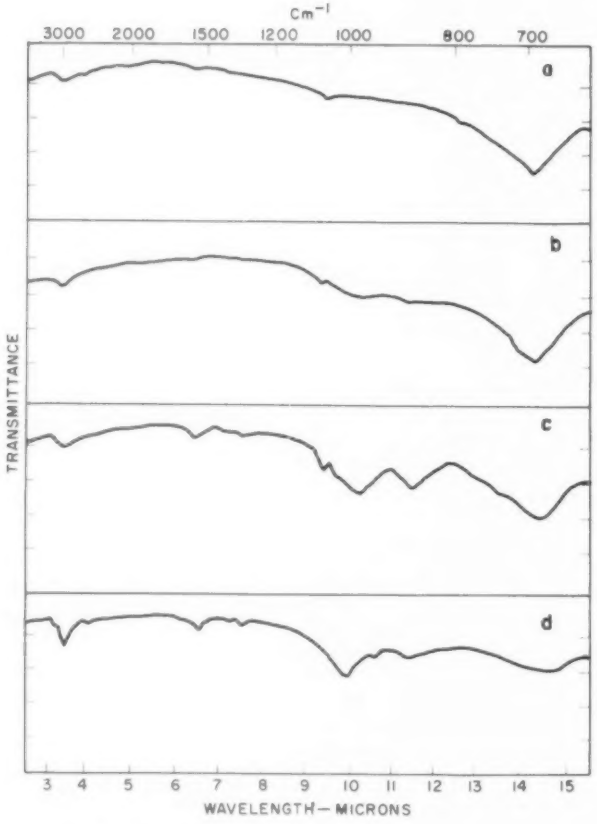

Fig. 12. Infrared absorption spectra.
a. Mg_2GeO_4 spinel form
b. $Mg_2(Ge,Si)O_4$ spinel form (25 mol% silicate)
c. $Mg_2(Ge,Si)O_4$ spinel form (38 mol% silicate)
d. $Mg_2(Ge,Si)O_4$ spinel form (47 mol% silicate)

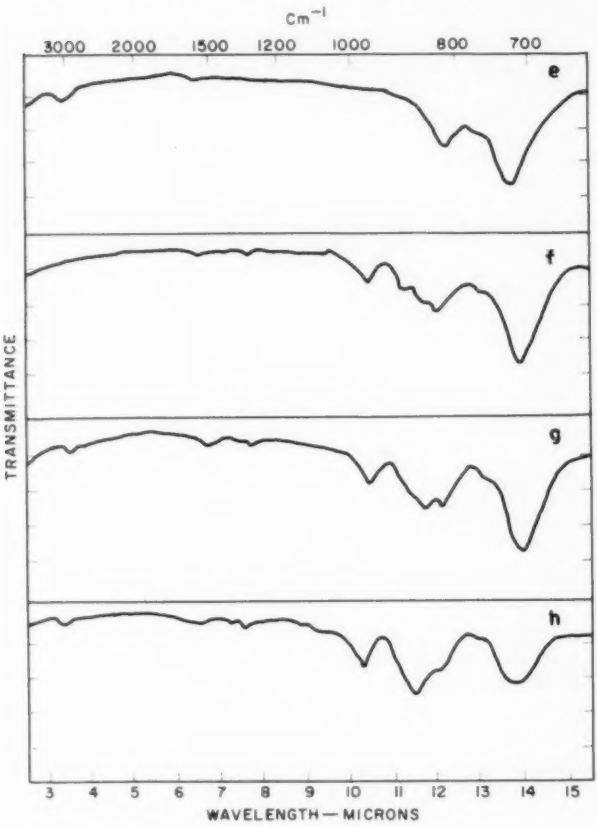

Fig. 13. Infrared absorption spectra

e. Mg_2GeO_4 olivine form
f. $Mg_2(Ge,Si)O_4$ olivine form (10 mol% silicate)
g. $Mg_2(Ge,Si)O_4$ olivine form (25 mol% silicate)
h. $Mg_2(Ge,Si)O_4$ olivine form (47 mol% silicate)

complex solids one can use the main absorption frequencies in the infra-red region to indicate primary coordination changes of the cations. Naturally the present substances presented excellent examples for checking such ideas. Figures 12, 13, and 14 present the infra-red absorption patterns for some of the spinel and olivine structure solid solutions. The following deductions are pertinent:

1. In Mg_2GeO_4 spinel all the Ge^{4+} is in 6 c.n. (cf. Ge-O absorption in $GeO_{2\ qtz}$ at 11.5 and in $GeO_{2\ rutile}$ at 14.0).
2. In both the olivine forms the Si and Ge ions appear to be of two types with

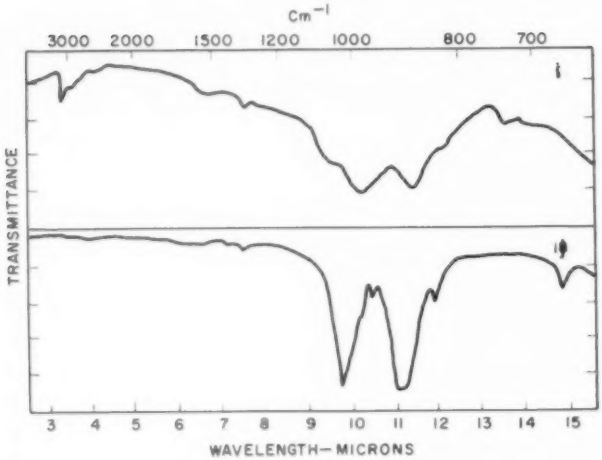

Fig. 14. Infrared absorption spectra
i. $Mg_2(Ge,Si)O_4$ olivine form (90 mol% silicate)
j. Mg_2SiO_4 olivine form

appreciably different Si-O (Ge-O) distances. Indeed the patterns themselves suggest the highly unlikely possibility of an inverse olivine structure.

3. Although this is not clearcut, the spinel solution towards the silicate member appears to be changing from an inverse to a normal spinel.

Unequivocal confirmation of the first deduction that Mg_2GeO_4 is an inverse spinel has been obtained from the x-ray intensities. In 1956 Durif-Varambon, Bertaut and Pauthenet came to precisely the opposite conclusion on the basis of intensities measured from a very poorly crystallized sample. They calculated that a distinctive criterion to judge between the various spinel arrangements is the ratios of the intensities of the 422 and 400 reflections. The following values were calculated:

$$\frac{I_{422}}{I_{400}} = \text{For Normal, 1.67; For Inverse, 6.6; For Random, 3.3}$$

Their conclusion was based on their measurement of the intensity ratio as 1.7. On examination of the ratio in random x-ray diffractometer mounts it was immediately noticed that the ratio was consistently very much higher than 1.7; indeed it never fell below 3.8 for the germanate end member, and values as high as 6.5 were found. Obviously it had not been possible to avoid all orientation in the slide preparations although the crystal size was extremely small. Since the more likely cubic habit or cleavage would tend to increase the 400 intensity in relation to 422 the true ratio $\frac{I_{422}}{I_{400}}$ is seen to approach if not equal the 6.6 figure for the inverse spinel.

With increasing Si^{4+} content there is a shift to lower values of the intensity ratios which suggests that as the Si^{4+} takes more tetrahedral positions the structure approaches the normal spinel.

Molar refractivity (Rm in cc/mole), table 4, affords another line of evidence on cation coordination. (Safford and Silverman, 1947; Roy, 1950; Dachille and Roy, in press b). The "measured" Rm of the olivine forms of Mg_2SiO_4 and Mg_2GeO_4 are 15.87 and 18.33 respectively, and each value is 0.4 less than the value calculated from the "ideal" values for component oxides. Similar small differences have been noted for binary and ternary compounds. In the olivines the Mg ions are in VI, and the Si,Ge ions are in IV coordination. The measured Rm for Mg_2GeO_4 spinel ($n = 1.768$) is 17.62, a value which is 1.09 less than that calculated for the normal spinel and 0.59 less than for the inverse. This latter value is comparable with the usual differences between observed and calculated values and suggests an inverse spinel Mg_2GeO_4. It can then be shown that the relative refractivity contribution of GeO_2 in the inverse spinel is about 14 percent less than that in a normal spinel, which difference is close to that found between the rutile and quartz forms of GeO_2.

TABLE 4

Molar Refractivities, Rm

Substance		Measured	Calculated	Difference
Mg_2SiO_4	olivine	15.87	16.27	.40
Mg_2GeO_4	olivine	18.33	18.71	.38
Mg_2GeO_4	inverse spinel	17.62	18.21	.59
Mg_2GeO_4	normal spinel	17.62	18.71	1.09

Values used for oxides (see Refs. cited for cation coordination)

Coordination	VI	IV
MgO	4.54	5.18
SiO_2	—	7.19
GeO_2	8.49	9.63

ACKNOWLEDGMENTS

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STABILITY RELATIONS OF GROSSULARITE AND HYDROGROSSULARITE AT HIGH TEMPERATURES AND PRESSURES*

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ABSTRACT. The equilibrium relations between hydrogrossularite + quartz and anorthite + wollastonite + water have been determined to 15500 bars and 810°C by means of the "simple squeezer" high-pressure apparatus. There is a continuous solid-solution series from grossularite, $3CaO \cdot Al_2O_3 \cdot 3SiO_2$, through hydrogrossularite to hibschite, $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The composition of hydrogrossularite, above 500°C and in equilibrium with quartz, is determined almost entirely by temperature. Grossularite is stable above 780° and 15 kilobars H_2O pressure in the presence of quartz.

INTRODUCTION

Pure grossularite garnet, $3CaO \cdot Al_2O_3 \cdot 3SiO_2$, is a very rare mineral in metamorphic rocks though members of the series grossularite-andradite are common, where some ferric iron replaces the aluminum. At modest temperatures and pressures in a hydrothermal environment hydrogarnets form (Yoder, 1950; Flint, McMurdie and Wells, 1941). Yoder succeeded in preparing hydrogrossularites of variable composition in hydrothermal experiments between 450°C and 750°C at pressures below 2000 bars. He failed to synthesize the dry end-member, grossularite, in the presence of water, and concluded that it could not exist in the presence of water at elevated temperatures. Later Coes (1954) synthesized grossularite at 600°C to 800°C and 15,000 bars. Yoder (1954) also prepared grossularite in the range below 750°C, 2000 bars and 1025°C, 10,000 bars. Unfortunately no further particulars are available.

Most naturally occurring hydrogrossularites form in metagabbros or in other rocks where silica is not present as a free phase. It seemed possible then that Yoder's earlier failure (1950) to synthesize the pure end-member, grossularite, was due to loss of silica to water vapor during the course of his hydrothermal run. This, indeed, was suggested by Yoder (1950) in his discussion of the results of his experiment. Fyfe and Turner (1958) found, however, that "if excess silica is present, grossularite will not form at low pressures between 450°C and 700°C, but that instead anorthite and wollastonite are the stable phases."

The present investigation was undertaken in the hope of clearing up some of these problems.

EXPERIMENTAL DETAILS

The majority of the experiments were carried out in the "simple squeezer" high-pressure apparatus designed by Griggs and Kennedy (1956). The confining pressure was produced by pressing two sintered carbide pistons together. The piston faces that come in contact had a diameter of approximately 6 mm. The finely ground sample, encapsulated in platinum foil was placed between the piston faces. The pistons were pressed together by a commercial 20-ton

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hydraulic jack, supported by a framework of plates and tie rods. The sample was heated by an external furnace enclosing the sample and pistons. Temperature was measured by a chromel-alumel thermocouple placed in a hole in the top piston in such a way that the tip of the thermocouple was approximately a quarter of an inch from the sample. The difference between temperature at sample position and temperature at the thermocouple junction was independently determined by calibration runs. Temperatures are believed to be accurate to $\pm$ 7°C.

Sintered chromium carbide pistons in Blackalloy piston holders were used. The pressure was determined from the force applied to the pistons, assuming that the sample is approximately under hydrostatic pressure. The pressure, measured in this way, under favorable circumstances is accurate to approximately 5 percent.

The starting material in the majority of the runs was a finely ground mixture of Allied Co. Reagent grade silicic acid, $SiO_2 \cdot nH_2O$, Baker's analyzed aluminum hydroxide and Baker's analyzed calcium oxide, with a 40 percent excess of silicic acid over stoichiometric proportions of a 1:1 grossularite-quartz mixture. The calcium oxide contained less than 0.04 percent iron. No great care was taken in weighing out the calcium oxide, for the presence of a little excess calcium along with a good deal of excess silica only meant that a little wollastonite was present in the runs on the grossularite side of the boundary, and the position of the boundary was not influenced. The products were identified by comparing x-ray patterns obtained on a Norelco high angle diffractometer.

The samples were made up of the powder and mixed with distilled water to form a paste. However, the presence or absence of added water did not affect the position of the equilibrium curve or the reaction rate. Apparently the silicic acid yields a sufficient amount of water on heating for the reaction to proceed normally.

The pressure was first raised to the desired value and this sample then heated. This ensured that little water was lost, and that, consequently, the water vapor pressure was equal to the total pressure (Kennedy, 1959). The time required to bring the sample to the desired temperature ranged from 15 to 40 minutes. Only a few seconds were required to bring the sample to pressure. After the sample had been held at the required temperature and pressure for approximately one half hour, the sample was quenched in an air jet. Temperature dropped from 800°C to 200°C in 3 to 4 minutes.

Considerable experience with the piston anvil device has shown that the rate of attainment of equilibrium in this apparatus is many times the rate in conventional hydrothermal gear. Presumably the strain energy stored in the sample as it is taken to pressure promotes very rapid recrystallization. The initial reaction rate in the piston anvil device is exceedingly high. However, after the sample has been to pressures and temperatures for approximately a half hour, the reaction rate is decreased so markedly that longer times make little difference. It has been our experience in this device that runs of one half hour or several days give essentially the same results. In this particular system a few runs of 24 hours duration were made. The results of these were identical with

the runs of half hour duration. It must be emphasized that this is not true with conventional hydrothermal gear.

RESULTS

The boundary between grossularite-hydrogrossularite + quartz and anorthite + wollastonite first studied by Fyfe and Turner (1958) has been worked out in considerable detail by us. Anorthite and wollastonite are stable on the low-pressure and high-temperature side of the boundary, while grossularite or hydrogrossularite and quartz are the stable phases at high pressure and low temperature. The end-member reaction is given by

$$3CaO \cdot Al_2O_3 \cdot 3SiO_2 + SiO_2 \quad CaO \cdot Al_2O_3 \cdot 2SiO_2 + 2\ CaO \cdot SiO_2$$

grossularite + quartz = anorthite + 2 wollastonite

The results of 85 runs are summarized in table 1. This table lists the temperatures and pressures of the experiments, the starting materials, and the products. Quartz and small amounts of wollastonite were present among the products of all runs, and therefore these two products are not listed in table 1. Presumably wollastonite was formed directly from calcium oxide and silica, even though the run was not in the anorthite-wollastonite field. Further, a little excess calcium oxide was probably present. All runs were made at 500°C or higher temperatures, as reaction rates were very slow at lower temperatures.

The boundary curve, shown in figure 1, has been drawn on the basis of

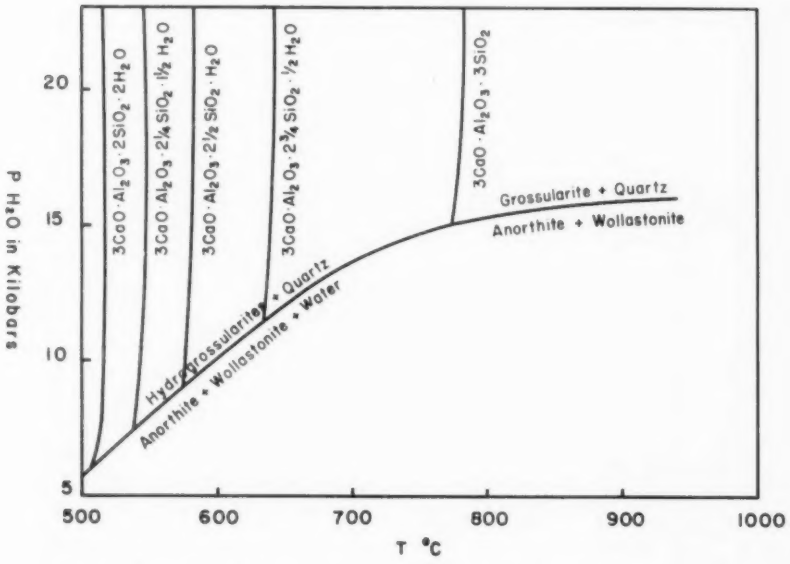

Fig. 1. Grossularite-hydrogrossularite relations at high temperatures and water pressures.

TABLE 1

Results

Run no.	Temp. °C ±7°C	Pressure kb ±1 kb	Time mins.	Unit-Cell of hydrogarnet Å ± .012	Result of x-ray examination of products	Starting materials
1	720	27	30	11.857	Gr.	Oxides + H_2O
5	845	14.3	30	11.851	An. + Gr.	"
8	700	5.05	30	—	An.	"
9	744	10.1	30	11.858	An. + Gr.	"
10	792	10.2	30	11.847 ± .018	An. + minor Gr.	"
11	847	10.1	30	—	An. + minor Gr.	"
12	690	10.2	30	11.874	An. + minor Gr.	"
13	639	10.1	30	11.888	Gr. + minor An.	"
14	639	4.97	40	11.890	Gr. + minor An.	"
15	587	4.95	60	11.902 ± .027	An. + minor Gr.	"
16	691	5.01	30	11.878	An. + Gr.	"
17	742	5.11	30	11.864	An. + minor Gr.	"
18	585	5.05	60	11.932	An. + Gr.	"
19	384	5.03	45	—	Boehmite	"
20	606	15.0	35	—	Gr.	"
22	698	14.8	30	11.857	Gr.	"
23	808	14.8	25	11.851	Gr. + minor An.	"
24	695	12.5	30	11.868	An. + Gr.	"
25	756	12.4	30	11.851, 11.852	An. + Gr.	"
26	687	14.7	60	—	Gr.	"
27	596	7.28	35	11.904	Gr. + minor An.	"
28	605	9.84	35	11.899	Gr. + minor An.	"
29	657	10.1	30	11.873	An. + Gr.	"
30	702	10.0	30	11.862	An. + Gr.	"
31	642	7.4	35	11.879	An. + Gr.	"
32	712	9.0	360	—	No crystallization	Dry Oxides
33	647	16.4	40	11.878	Gr.	Oxides + H_2O
34	608	16.9	40	11.892	Gr.	"
35	657	12.9	35	11.877	Gr.	"
36	602	13.3	35	11.907	Gr.	Hydroxides
37	549	10.2	60	11.907	Gr.	Oxides + H_2O
38	503	10.6	60	11.988	Gr.	"
39	687	14.0	30	11.859	Gr.	"
40	708	14.4	30	11.867	Gr.	"
41	719	14.1	30	11.858	Gr.	"
42	754	14.3	30	11.855	Gr. + minor An.	"
43	697	10.6	30	11.884	An. + Gr.	Oxides + H_2O (insufficient silica)
44	620	10.8	30	11.925	Gr.	"
49	625	12.6	20	11.881	Gr.	Oxides + H_2O
52	615	13.1	30	11.895	Gr.	Oxides + H_2O (large excess silica)
53	625	13.2	30	11.912 ± .022	Gr.	"

TABLE 1 (Continued)

Run no.	Temp. °C ±7°C	Pressure kb ±1 kb	Time mins.	Unit-Cell of hydrogarnet Å ± .012	Result of x-ray examination of products	Starting materials
54	697	13.0	30	11.877	An. + Gr.	Oxides + H_2O
55	633	13.5	30	11.900	Gr.	"
56	596	20.9	30	11.909	Gr.	"
57	516	21.9	30	11.966	Gr.	"
58	573	21.0	40	11.912	Gr.	"
59	550	22.1	30	11.948	Gr.	"
60	570	17.9	30	11.924	Gr.	"
61	505	18.9	30	11.956	Gr.	"
62	576	15.3	30	11.916	Gr.	"
63	500	16.3	30	11.997 ± .022	Gr.	"
64	560	13.1	35	11.930	Gr.	"
65	502	14.0	35	12.019 ± .022	Gr. + Boehmite	"
66	555	7.9	40	11.948 ± .018	An. + Gr.	"
67	500	8.4	40	12.035 ± .031	Gr. + Boehmite	"
68	556	6.0	45	11.939 ± .037	An. + Boehmite + Gr.	"
69	500	6.4	45	12.045 ± .067	Boehmite + Gr.	"
70	666	10.7	30	11.872	An. + Gr.	"
71	600	11.4	30	11.903	Gr.	"
72	687	12.7	40	11.867	An. + Gr.	"
73	672	13.4	40	11.867	Gr.	"
74	819	16.6	25	11.851	Gr.	"
75	778	16.7	45	11.853	Gr.	"
76	803	15.6	35	11.853	Gr.	"
77	762	15.7	35	11.856	Gr.	"
78	826	5.3	45	11.856	Gr.	"
79	909	5.3	30	11.855 ± .022	An. + minor Gr.	"
80	610	10.5	30	11.898	Gr.	"
81	584	9.4	30	11.916	An. + Gr.	"
82	535	5.21	120	—	An. + Gr.	"
83	535	7.65	75	11.923 ± .022	Gr.	"
85	654	11.8	30	—	Gr.	"
86	510	5.4	120	11.973 ± .044	An. + Gr.	"
87	720	14.1	40	—	An. + Gr.	"
88	809	15.3	25	—	Gr.	"
89	677	13.0	30	—	An. + Gr.	"
90	514	6.1	120	12.021 ± .044	An. + Gr.	"
91	585	10.0	20	11.928	Gr.	Anorthite + Wollastonite + H_2O
92	585	10.0	20	11.930	Gr. + minor An.	Oxides H_2O
93	622	10.0	20	—	An. + Gr.	Anorthite + Wollastonite + H_2O
94	622	10.0	20	11.903	An. + Gr.	"
100	735	13.9	45	—	An. + minor Gr.	"
101	660	14.3	45	—	Gr. + minor An.	"
103	717	14.0	50	—	An. + Gr.	"
104	705	14.3	50	—	Gr. + minor An.	"

runs plotted in the p-t field in which anorthite formed and runs in which no anorthite formed. Runs of varied durations gave consistent results. All samples were quenched under pressure so that the sample remained on the grossularite side of the boundary during quenching.

An attempt was made to reverse the boundary by approaching equilibrium from the high temperature rather than the high pressure side. Runs 92, 94, 103 and 104 were made using a starting mixture of finely ground anorthite and wollastonite. Unfortunately, some grossularite was formed in these runs as the garnet stability field must be crossed while bringing the runs to temperature and pressure, so results were not clear-cut. However, runs made on the high pressure side of the boundary curve in the grossularite field showed a large yield of grossularite, while a much smaller yield of grossularite was obtained on the high-temperature side of the boundary curve. Thus the reversibility of the curve shown is believed established.

Yoder (1950) found that at very high temperatures grossularite breaks down to gehlenite, wollastonite and anorthite. Gehlenite was not detected in any of the present runs. Temperatures were not sufficiently high in the present experiments to be in the gehlenite stability field as extrapolated from Yoder (1950) and it is further unlikely that gehlenite has a stability field in the presence of free quartz, where the reaction gehlenite plus quartz equals wollastonite plus anorthite may be expected.

The crystals of grossularite-hydrogrossularite, formed by the reaction, were very small and it was impossible to determine their refractive indices accurately in order to establish the extent of substitution of water for silica in the grossularite-hydrogrossularite "molecule". Consequently, x-ray techniques were employed to measure the dimensions of the unit-cell of the "grossularite" obtained in each run.

Sodium chloride was standardized against diamond ($a_o = 3.56680 \pm 0.0001$ Å). NaCl has a strong peak 2° from the strongest peak of grossularite for CuK_α radiation. The unit-cell size of the hydrogrossularite and grossularite formed in the various runs were measured by x-raying the samples on a Norelco diffractometer with a scanning of 1/8° per minute, using the pre-calibrated sodium chloride as an internal standard. In all cases the (420) peak of the garnet was used for measurement. For any given run, the unit-cell edge obtained is reproducible to 0.004 Å. However, a second run made at the same temperature and pressure did not usually yield exactly the same value. This was probably due to small differences in the conditions of the runs. However, in the majority of cases the a_o-values given in table 1 are accurate to better than 0.012 Å. There are exceptions for runs at very low temperatures (below 550°C), where the reaction rate was very slow, and for runs at very high temperatures but low pressures, where only a little metastable grossularite might be produced. In these cases a rather low yield of hydrogarnet is encountered, which makes an accurate determination of a_o difficult. Furthermore, the peaks tended to broaden as lower temperatures were approached, suggesting a range of composition within a run or poor crystallization.

Pabst (1942) found that the hydrogrossularite, hibschite, is octahedral with a unit-cell edge of 12.0 Å. The unit-cell edge of the dry end-member,

grossularite, is 11.851 Å (Skinner, 1956).

The composition of hydrograssularite at a given temperature is, as a first approximation, nearly independent of pressure. Thus, under the conditions of our experiments, composition of garnet and unit-cell size can be closely correlated with temperature of formation. Variation of cell size as a function of temperature is shown in figure 2. The length of the vertical lines in figure 2

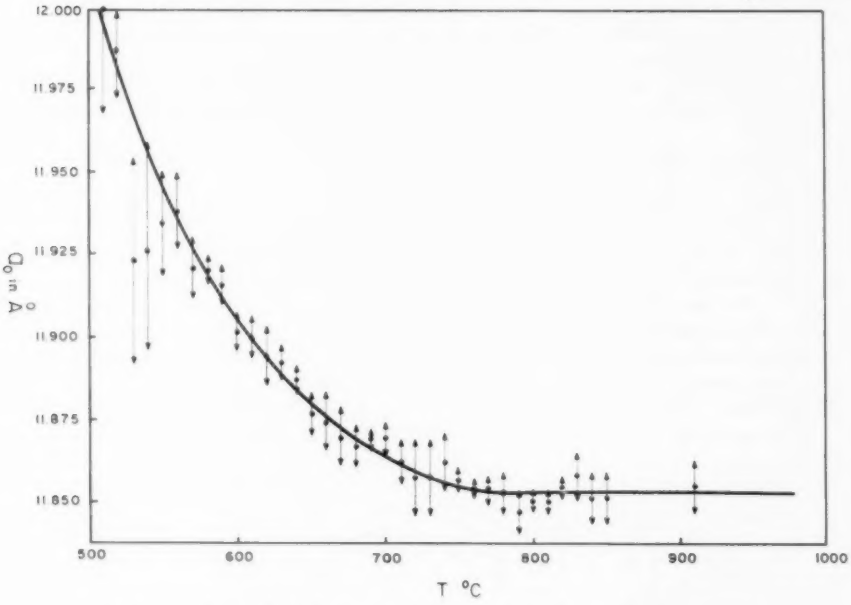

Fig. 2. a_o of grossularite-hydrogrossularite, synthesized at various temperatures.

show the estimated uncertainty in cell sizes determined from all runs within 20° of the temperature plotted.

The curve separating the fields of grossularite-hydrogrossularite plus quartz and anorthite plus wollastonite plus water is not a straight line in the p-t plane, but its slope decreases with higher temperatures, for the composition of the hydrograssularites changes regularly with temperature. Above 780° all grossularites formed had a cell of approximately 11.850 Å and were presumed to be pure dry end-members. The curve appears to be a straight line in this region within the limits of experimental error.

Composition boundaries of the various hydrograssularites, shown in figure 1, have been plotted from the smoothed curve of figure 2 by use of Vegard's law (Vegard, 1927) and by assuming that the value 12.0 Å (Pabst, 1942) is correct for pure hibschite. There is no break in the smoothed curve of figure 2 which corresponds to the hibschite composition. Thus the mineral hibschite exists only as an intermediate member of a solid-solution series. It forms, when

the water vapor pressure is above 6000 bars, in the presence of excess quartz, at 510 ± 15°C.

The unit-cell size of grossularite, obtained from the average of all runs above 780°C, is 11.852 Å. This agrees well with the determination by Skinner (1956) of the unit-cell of pure grossularite, 11.851 Å.

Belyankin and Petrov (1941) showed that when hibschite was heated at one atmosphere, a strong endothermic reaction occurred at 650°C. The effect is apparently not reversible and they suggest that the transition is "from the original crystalline phase into an amorphous phase". Skinner (1956) pointed out that this reaction probably corresponds to a breakdown of hibschite, presumably into amorphous components, and a loss of water.

However, hibschite does not totally break down at the higher H_2O pressures of our experiments, but undergoes a reaction which may be represented as

$$3CaO \cdot Al_2O_3 \cdot (SiO_2)_{m_1} \ (H_2O)_{6-2m_1} + (m_2 - m_1)\ SiO_2$$
$$\rightleftarrows 3CaO \cdot Al_2O_3 \cdot (SiO_2)_{m_2} \ (H_2O)_{6-2m_2} + 2(m_2 - m_1)H_2O$$

where m_1 and m_2 are numbers between 0 and 3. Hibschite and grossularite are represented by the special cases where m equals 2 and 3, respectively.

All runs, with the exception of runs 91-94, were made in the piston-anvil device described by Griggs and Kennedy (1956). Runs 91-94 were made in a large bomb fitted with an internal furnace capable of pressures to 10 kilobars. The pressure medium was argon gas and samples were sealed in small platinum envelopes. Runs 91 and 93 were made using a mixture of oxides and water as starting material. Runs 92 and 94 were made on a starting material of finely powdered anorthite and wollastonite and water. Results of these runs (see table 1) confirmed the position of the curve and equilibrium composition of garnets as determined by the piston-anvil device. It is interesting to note that the value for a_0 of the garnet, produced from a starting mixture of anorthite and wollastonite in run 92, was the same as those produced from a starting mixture of the oxides in run 91 and thus independent of the direction of the approach to equilibrium.

Runs 43 and 44 were made with less than stoichiometric amounts of silica for grossularite. The hydrogrossularite showed a much larger water-silica ratio than hydrogrossularites made at similar temperatures and pressures where quartz was present as a free phase. Our runs indicate that hydrogrossularite will not form above 780°C if free quartz is present. Even in the presence of large amounts of excess silica, they form with expected composition at all temperatures below 780°C if water vapor pressure is sufficiently high. Run 32 was made with an anhydrous mixture of oxides with hope of preparing grossularites below 780°C. No crystallization was observed after six hours at 712°C and 9 kilobars confining pressure.

The entropy change, Δs, and heat of transition, Δh for the reaction hydrogrossularite plus quartz equals anorthite plus wollastonite plus water can be estimated from the slope of the equilibrium curve, shown in figure 1. The slope of this curve changes with temperature and pressure as the composition of hydrogrossularite changes with temperature and pressure. Thus this boundary

possesses neither the typical form of a hydration-dehydration boundary nor of a solid-solid reaction boundary (Kennedy, 1954). The slope of the boundary curve was determined graphically at intervals of approximately 50°, and Δv, Δs, and Δh were calculated for the series of temperatures. These results are shown in table 2. It was necessary to estimate the molar volumes of the various

TABLE 2

Thermochemical Data for the Reaction Hydrogrossularite + Quartz = Anorthite + Wollastonite + Water

P kb	T °C	a_o Å	$\frac{dP}{dt}$ bars/degree	Spec. vol. of water cc/gm.	ΔV cc/mole reaction	ΔS cal/deg. mole reaction	Δh k cal/ mole re-action
6.2	510	11.995	45.0 ± 15	1.100	87.6	94 ± 30	74 ± 23
8.0	550	11.944	42.4 ± 8	1.047	81.2	82 ± 16	67 ± 13
10.0	600	11.905	40.2 ± 8	1.018	77.4	74 ± 15	65 ± 13
12.0	650	11.880	38.1 ± 6	.993	75.4	69 ± 12	64 ± 11
13.7	700	11.864	27.4 ± 6	.978	74.4	49 ± 11	48 ± 11
14.7	750	11.855	17.1 ± 6	.971	73.9	30 ± 11	31 ± 11
15.1-15.4	780-820	11.852	$8.6\ ^{+4.4}_{-2.6}$	—	73.7	$15.2\ ^{+8}_{-5}$	$16.3\ ^{+8.6}_{-5.3}$ at 800°C

phases at each of the temperatures involved in the calculation. Differences in compressibility and thermal expansion of the various solid phases were assumed negligible and disregarded, since the major uncertainty in the calculations was that of the graphical determination of the instantaneous slope of the equilibrium curve at various temperatures. The specific volume of the hydrogrossularite was computed from the x-ray measurements of unit-cell size. No experimental data were available for the specific volume of water at pressures and temperatures of this reaction. However, Knopoff, Holser and Kennedy (unpublished data) have prepared tables of the specific volume of water by use of a Thomas-Fermi-Dirac type equation of state to interpolate between the specific volumes of water at lower pressures and specific volumes of water at extreme pressures, as found by shock wave methods. The measured values of Δv and dp/dt, with derived values of Δs and Δh, are listed in table 2.

It is clear that in an anhydrous environment, where the only pressure is confining pressure, hydrogrossularites cannot form. Under such circumstances the reaction would be anorthite plus wollastonite equals grossularite plus quartz. The curve for this reaction then is the prolongation of the boundary found above 780°C. This curve intersects the 0°C axis at a pressure of approximately $8.4\ ^{+2.5}_{-4.0}$ kilobars. Thus within these limits of error, pure grossularite is unstable in the presence of quartz with respect to anorthite and wollastonite at all pressures under 8 kilobars. It probably cannot form in the Earth's crust

at pressures of less than 9-11 kilobars, due to the geothermal gradient (Birch, 1955). This corresponds to a depth of somewhat more than 30 kilometers and suggests a much higher pressure environment for grossularite than is generally estimated.

CONCLUSIONS

Grossularite is associated either with wollastonite or with anorthite in the metamorphism of impure calcareous rocks. Anorthite and wollastonite seem to be imcompatible in most instances (Harker, 1939). Thus the majority of field observations agree with the phase diagram as presented in this paper.

Some exceptions are known, however. In the Carlingford District (Osborne, 1932) and in Deeside (Harker, 1939) wollastonite and a lime-bearing feldspar are found in close association, with or without grossularite. From the evidence of our phase diagram, it may be presumed that these rocks were formed at high temperatures and low pressures. Rocks with wollastonite, grossularite and anorthite can only form close to the equilibrium curve or form where there is insufficient silica for the various reactions to run to completion.

Yoder (1950) suggests that the majority of garnets described as grossularites are in fact members of the hydrogrossularite series. Under the very rare geological circumstances where the total pressure is equal to the partial pressure of water, pure grossularite cannot form under 780°C, but under most conditions the partial pressure of water is believed less than the total confining pressure. Thus pure grossularites can form at any temperature if the confining pressure is sufficiently high, that is, above the prolongation of the grossularite boundary shown in figure 1.

Unfortunately, the phase diagram we present cannot be applied directly to many geological circumstances. Natural grossularite usually contains other ions, especially trivalent ions, and the influence of these other ions on the stability field of grossularite is unknown. Similarly the reaction we discuss is that of anorthite plus wollastonite equals grossularite plus quartz. Normally a lime-bearing feldspar is involved in the natural reaction and the equilibrium position of the boundary will be influenced by an unknown but appreciable amount by the sodium in the feldspar. The reaction with soda feldspars will be one in which jadeite is an additional high pressure product formed and a complete understanding of this equilibrium involves further experimentation. Further, if free quartz is not present and similarly the partial pressure of water is low, pure grossularites will be stable to much lower temperatures and pressures than indicated on our phase diagram.

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SILURIAN STRATA OF THE KLAMATH MOUNTAINS, CALIFORNIA

MICHAEL CHURKIN, JR.[1] and RALPH L. LANGENHEIM, JR.[2]

ABSTRACT. A eugeosynclinal suite comprising shale, volcanic graywacke, quartz arenite, bedded chert, limestone and tuff crops out along Willow Creek, west of Gazelle, California. The limestone and associated interbeds of shale contain Silurian trilobites, brachiopods and corals. The bulk of the sequence, however, consists of unfossiliferous sedimentary rocks beneath the limestone. Trilobites in the limestone belong to genera previously reported from eastern North America, but the assemblage appears most closely related to Middle and Upper Silurian faunas of Alaska and Asia.

Silurian sedimentary rocks are succeeded in thrust fault contact by phyllite and semischist in the western part of the area. These metamorphic rocks have been derived from sedimentary rocks similar to those of the Silurian sequence chiefly by regional cataclastic deformation. Small bodies of diorite and quartz diorite and a large pyroxenite-peridotite pluton intrude both the sedimentary and metamorphic rocks. In addition Tertiary and/or Quaternary basalt flows and alluvium locally truncate all older rocks.

Relatively open folds and high-angle faults generally trending north characterize structural patterns within the sedimentary rocks in marked contrast to a complex pattern of crumpling and shearing in the strongly lineated metamorphic rocks. In addition the thrust plane is deformed by broad open folds plunging gently northwest. Thus it is possible to infer at least three periods of diastrophism in this area.

INTRODUCTION

This paper describes rocks cropping out near the eastern edge of the Klamath Mountain province, where lavas of the Cascade Range overlap Paleozoic rocks. Meagre knowledge of the early Paleozoic sequence that underlies a wide region in the eastern Klamath Mountains of central Siskiyou County invites investigation. Thus in the summer of 1957 a detailed study was made of an isolated fossiliferous limestone body cropping out near Gazelle, California (fig. 1). This work was undertaken in an attempt to determine the age of the limestone and to explain its origin and distribution. In addition to progress made with these problems, discovery of a folded thrust fault seems of sufficient interest to warrant publication.

Field work was conducted primarily by Churkin during the summer of 1957. Additional mapping to verify existence of the thrust fault was conducted by both writers during two later periods of approximately a week each in winter and spring of 1958.

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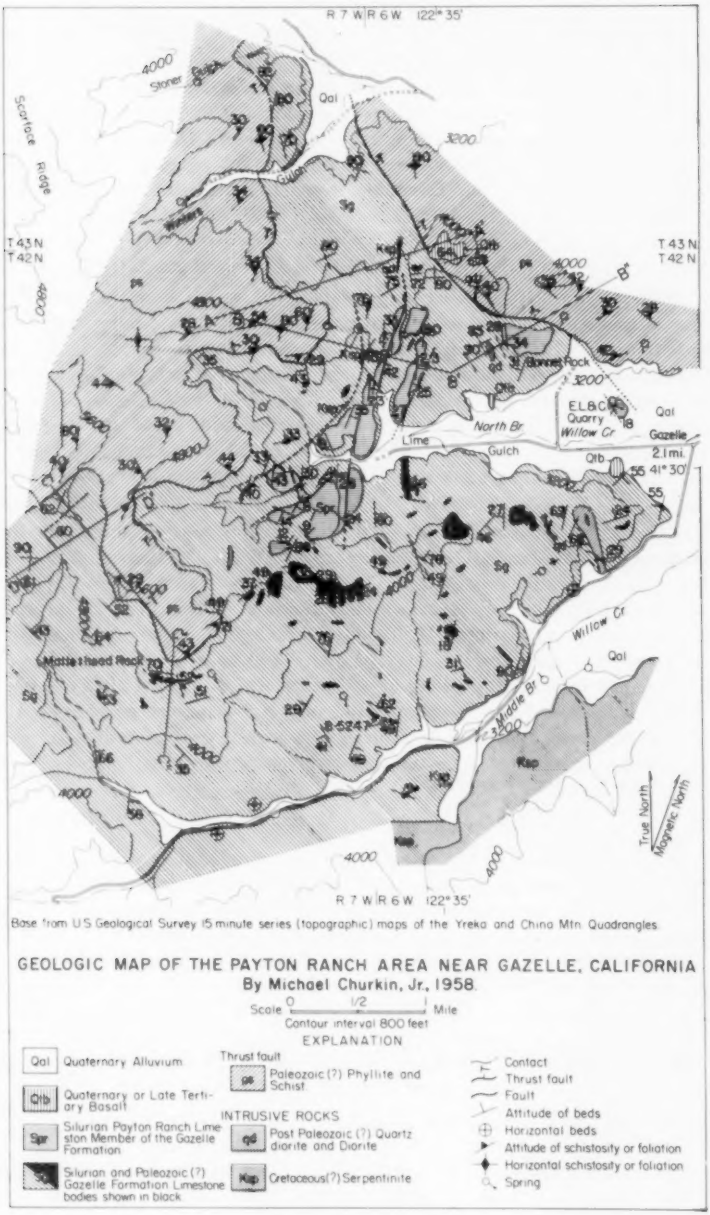

Base from U.S. Geological Survey 15 minute series (topographic) maps of the Yreka and China Mtn. Quadrangles

GEOLOGIC MAP OF THE PAYTON RANCH AREA NEAR GAZELLE, CALIFORNIA

By Michael Churkin, Jr., 1958

Scale 0 1/2 1 Mile

Contour interval 800 feet

EXPLANATION

Qal Quaternary Alluvium

Qtb Quaternary or Late Tertiary Basalt

Spr Silurian Payton Ranch Limestone Member of the Gazelle Formation

Sg Silurian and Paleozoic (?) Gazelle Formation Limestone bodies shown in black

Thrust fault

ps Paleozoic (?) Phyllite and Schist

INTRUSIVE ROCKS

qd Post Paleozoic (?) Quartz diorite and Diorite

Kap Cretaceous(?) Serpentinite

Contact

Thrust fault

Fault

Attitude of beds

Horizontal beds

Attitude of schistosity or foliation

Horizontal schistosity or foliation

Spring

Fig. 1. Geologic map.

PREVIOUS WORK

In an early report (Diller, 1886) C. D. Walcott assigned a "*Lithostrotion*" collected by J. S. Diller at Willow Creek to the Carboniferous. Later Diller, with Charles Schuchert in 1894 published a brief description of the rocks cropping out along Willow Creek southwest of Gazelle. Corals collected here from limestone were identified as Devonian by Schuchert (Diller, J. S. and Schuchert, 1894) and this limestone near Gazelle was subsequently referred to as a northern extension of the Devonian Kennett Formation of the Redding Quadrangle (Diller, J. S., 1906). Stauffer (1930) also described corals collected 3½ to 4 miles southwest of Gazelle as Devonian. Averill (1931) briefly describes the rocks in the area, but reports no additional fossils.

Merriam (1940) collected an assemblage of fossils from the rocks along Willow Creek, 3½ miles southwest of Gazelle and identified them as Silurian. Furthermore he compared his fossils with collections in the U. S. National Museum made by Diller and reports that the two collections "undoubtedly represent approximately the same zones" (Merriam, 1940, p. 48). It is also likely that Stauffer's material came from the same locality and that this spot is the same as our locality B-5247 NW 1/4, SW 1/4, NW 1/4, Sec. 19, T. 42 N., R. 6W., China Mountain quadrangle, on the Creshew Ranch.

Heyl and Walker (1949) map most of the area in support of an evaluation of the limestone deposits but do not distinguish the metamorphic rocks from unmetamorphosed detrital sedimentary rocks. Wells, Walker and Merriam (1959) have recently described and named the Upper Ordovician (?) Duzel formation and Upper Silurian Gazelle formation in this area. This report, which consists of a description of these two formations in their regional aspect and a reconnaissance geologic map of about 400 square miles including the total known outcrop of the newly named units, was published after our paper had been submitted for publication. Thus only a few references have been inserted in the present discussion in order to integrate our more detailed study of a much smaller area into the regional relationships outlined by Wells, Walker and Merriam (1959).

STRATIGRAPHY AND PETROGRAPHY

Gazelle Formation.—The interbedded sequence of shale, sandstone, bedded chert, conglomerate, limestone and tuff in the Gazelle area is here referred to as the "Gazelle Formation" of Wells, Walker and Merriam (1959). Shale and sandstone predominate in the Gazelle Formation, but lateral gradation from one lithologic type to another is widespread and bedded chert, conglomerate and limestone occur abundantly as discontinuous lenses and layers. A single outcrop of andesitic lapilli tuff near locality B-5247 is the only evidence of volcanic rock in the Gazelle formation noted in the course of this study. The Gazelle Formation crops out in the central portion of the area (fig. 1) and forms the east-west trending ridge between the North and Middle Branches of Willow Creek (figs. 1 and 2).

A thick, fairly continuous limestone layer, dissected by erosion and repeatedly faulted, dominates the central part of the area forming cliffs and bold outcrops. This unit is the only member of the Gazelle Formation that is trace-

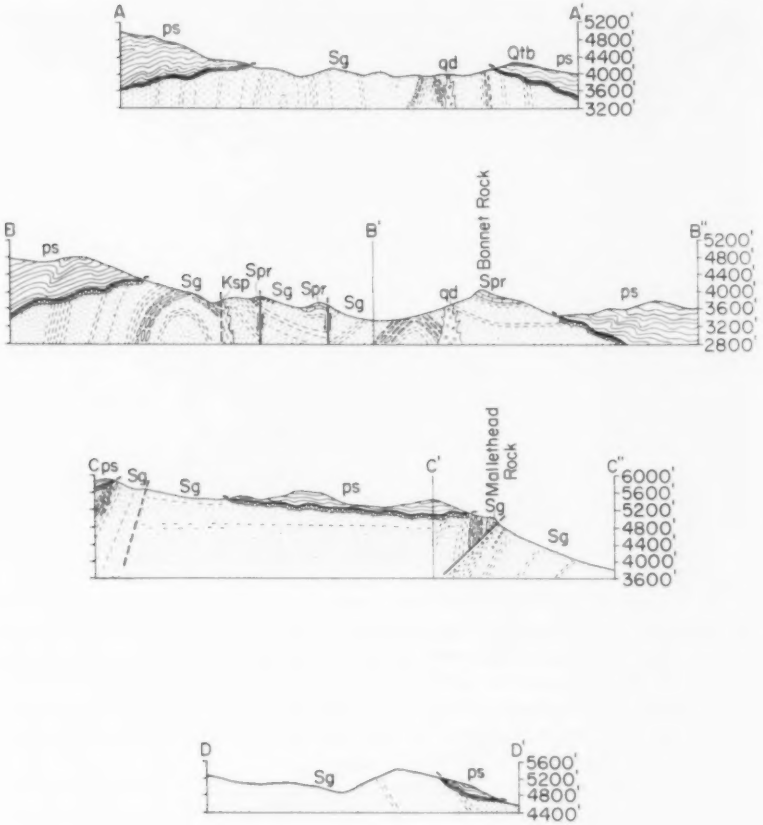

Fig. 2. Structure sections.

able for significant distances and is herein named the "Payton Ranch Limestone Member" of the Gazelle Formation. Outcrops on the east side of the high peak (elev. 4320 feet) in the NE 1/4, SW 1/4, Sec. 6, T. 42 N., R. 6 W., Yreka Quadrangle, Siskiyou County, California are designated as the type locality. The relationship between the Payton Ranch Limestone and rocks below it is well established. Over 600 feet of shale, sandstone, bedded chert, conglomerate and scattered lenses of similar limestone occurs stratigraphically below the member. The upper contact, however, is everywhere either an erosion surface or a fault contact. Some of the Gazelle Formation outcrops west of the Payton Ranch Limestone exposures are, however, possibly younger than the member.

The base of the Payton Ranch Limestone Member is thin-bedded and contains thin interbeds of shale. Above the thin-bedded, basal portion, however, the limestone is poorly stratified, very thick-bedded, fairly pure calcium carbonate. Excepting local intra-formational conglomerate and brecciated, recrystallized areas along faults, the limestone is finely crystalline or microcrystalline. Most of the limestone is sparsely fossiliferous containing corals, brachiopods, crinoid stems and echinoderm fragments. Some is bioclastic limestone. These fragmentary fossils have nearly the same composition as the fine-grained, crystalline, calcite matrix and, therefore, fossils generally do not stand out in relief on pitted and fluted weathered surfaces.

Lenses of limestone occur stratigraphically below the Payton Ranch Limestone and form small outcrops in the southern portion of the area. In contrast to the Payton Ranch Limestone, these lenses are mostly thin-bedded and the limestone is less pure. Some beds contain intermixed chert pebbles and sand while others are interbedded with lenses of gray-black chert. At the extreme eastern tip of the divide between the North and Middle Branches of Willow Creek, outcrops of dark-gray, thin-bedded limestone contain shale laminae. An oolitic limestone crops out along the hill above this limestone and is itself overlain by calcareous quartz arenite.

Portions of the oolitic limestone are composed of oolites and pisolites cemented together by microcrystalline calcite. Oolites occur in the centers of some pisolites, but others have microcrystalline calcite nuclei. The centers of most of the oolites, however, are replaced by large calcite or quartz crystals, but the outer microcrystalline concentric laminae are well-preserved. Many smaller oolite-like bodies (under 0.3 mm), lacking laminar structure, may be fecal pellets.

Limestone conglomerate underlain by shale and graywacke crops out extensively along the top of the divide between the North and Middle Branches of Willow Creek (fig. 3). This rock is mostly composed of rounded to subangular boulders and pebbles of limestone in a matrix of gray-black, coarse sand. Scattered angular fragments of sandstone and shale up to 2 feet in diameter also occur here. This type of conglomerate grades eastward and westward into conglomerate composed solely of limestone fragments cemented with light-gray calcite. The size, angularity, and poor sorting of the detritus composing the conglomerate require a nearby source. Close association with the Payton Ranch Limestone together with lithologic similarity of the limestone

Fig. 3. Limestone conglomerate in the Gazelle Formation, Sec. 13, T. 42 N., R. 7 W. on the divide between the North and Middle Branches of Willow Creek. The boulders, cobbles and pebbles of limestone and sandstone are in a matrix of gray-black coarse sandstone.

boulders to the limestone in the Payton Ranch Limestone suggests that the conglomerate results from local reworking of the Payton Ranch Limestone.

Lenses of thin-bedded gray to black chert are interbedded with graywacke and shale. The chert consists mostly of very fine-grained crystalline silica transected by scattered, clear veinlets of chalcedony and coarser quartz. Abundant argillaceous material is present, however, in some thin, impure, chert beds described best as porcellanite. In places the chert is intensely crumpled, crushed and recemented with silica.

Most of the shale in the area is either brown, black or red. It is generally silty and contains thin interbeds of sandstone and siltstone. Slaty cleavage and fracturing which locally produce pencil structure are characteristic. Outcrops, however, are generally thoroughly covered by thick soil and vegetation.

Two contrasting sandstones crop out in the area. Volcanic graywacke is widespread stratigraphically below the Payton Ranch Limestone in the central portion of the area, but calcareous siltstone and quartz arenite are prominent on the ridges in the southeastern and far western portions of the area.

The volcanic graywacke is a very hard, dark-gray almost black sandstone which is interbedded with silty shale and bedded chert. Characteristically the graywacke is thick-bedded, poorly stratified, and contains scattered angular pebble-sized fragments of argillite and chert. Graded bedding is uncommon and the poor sorting and lack of stratification gives the impression that the graywacke accumulated as a "poured-in" type of sediment. The lower contact of the graywacke, shale and chert sequence is unknown, but the graywacke gen-

erally grades upward into shale interbedded with thin beds of limestone at the base of the Payton Ranch Limestone.

Microscopically the graywacke is composed of an unsorted aggregate of subangular grains imbedded in a green microcrystalline chloritic matrix. Most grains are volcanic rock fragments, but polysynthetically twinned albite and subordinate amounts of chert and argillite also are present. Quartz grains and ilmenite which is almost completely altered to leucoxene, comprise about 5 percent of the rock. The volcanic rock fragments are readily distinguishable by their texture of subparallel plagioclase microlites in an altered groundmass of green chloritic material. Diagenetic alteration of detrital grains and recrystallization of the matrix are clearly indicated, in thin sections. Most of the albite grains are penetrated by minute flakes of chlorite and sericite and are also partially replaced by calcite. Interstices between the grains are occupied by pale-yellowish-green chloritic material containing shreds of sericite which replaces the margins of the grains. Replacement of detrital grains by matrix minerals shows that the matrix is recrystallized (Williams and others, 1955, p. 298).

The high percentage of volcanic rock fragments in the graywacke and the deficiency of quartz indicate that the detritus was derived from intermediate or basic volcanic rocks. The smaller amount of material from chert and argillitic rock suggests a minor source in sedimentary terrain. Both keratophyres and spilitic basalts are characterized by feldspars principally in the albite range. However, it is suggested that the highly altered grains of albite in the graywacke are products of diagenetic alteration of more calcic plagioclase. Thus it is proposed that normal andesitic or perhaps basaltic volcanic rocks were the chief source of detrital grains.

Quartz arenite crops out in the southeastern portion of the area and underlies phyllite and semischist along the western edge of the area. Many beds in the southeast outcrop area are thinly cross-laminated and contain interbeds of shale, siltstone, chert and limestone. The quartz arenite is fairly well sorted, and most of the grains are subangular to subrounded. Quartz comprises about 90 percent of the total detrital constituents and grains of chert, albite, muscovite, ilmenite, leucoxene, zircon, and magnetite make up the remainder. The quartz arenite is well compacted as the quartz grains are in close contact with deformed flakes of muscovite pinched between them. Secondary calcite and rhombs of dolomite partially replace and cement the detrital grains.

A marked difference in degree of maturity exists between the volcanic graywacke and the quartz arenite. The immature volcanic graywacke is poorly sorted and consists largely of unstable volcanic rock fragments and grains of albite. In contrast, the quartz arenite is moderately sorted, and except for a minor amount of albite, contains only the most stable minerals—chiefly quartz with accessory muscovite, zircon, leucoxene and magnetite.

Gray-black chert conglomerate locally underlies the Payton Ranch Limestone. Generally, this chert conglomerate grades upward into sandstone and calcareous shale at the base of the limestone. In places, however, the conglomerate is directly succeeded by limestone and pebbles of chert occur within the limestone several feet above its base. The conglomerate is only vaguely strati-

fied and locally is poorly sorted, containing pebble-sized fragments of chert in a sandy matrix. Chert is the most abundant detrital constituent of the conglomerate and locally comprises almost 100 percent of the pebbles. Subordinate amounts of argillite and quartz pebbles are locally intermixed with the chert pebbles. Most pebbles are rounded but the sand and silt grains of the matrix are generally subangular. Where the conglomerate is well-sorted and has no matrix, the pebbles are cemented by iron-stained siliceous material producing a very hard rock which breaks across the pebbles.

Three partial sections of the Gazelle Formation will serve to show the abrupt lateral gradations between rock types within the formation (fig. 1). These sections define a northwest-southeast line across the east-central portion of the area and are spaced less than a mile apart. Each includes the Payton Ranch Limestone at the top which serves to establish the physical lateral equivalence of the rock below.

I Section measured on the east side of the highest peak (elev. 4320 feet) capped with limestone (NE 1/4, SW 1/4, Sec. 6, T. 42 N., R. 6 W., Yreka Quadrangle, Siskiyou County, California).

Unit	Description	Thickness in feet
	Gazelle Formation, top and bottom not exposed.	
	Payton Ranch Limestone Member (Type Section)	
7	Limestone, finely crystalline, light-gray to dark-gray, very thick-bedded, massive, sparsely fossiliferous; top removed by erosion.	171
8	Shale, calcareous, brown, thinly interbedded with limestone; abundant corals.	17
	Undifferentiated Gazelle Formation	
5	Graywacke, coarse-grained, dark-gray, poorly stratified; grains predominantly volcanic rock particles. Contains lenses and boulders of limestone.	41
4	Limestone, finely crystalline, sandy, dark-gray, thinbedded.	28
3	Graywacke, very coarse-grained, pebbly, poorly stratified; grains predominantly volcanic rock particles.	37
2	Shale, black, silty, highly fractured.	34
1	Bedded chert, dark-gray, with thin interbeds of pebbly, calcarenite; base unexposed.	14
	Total	342

II West flank of Bonnet Rock, SE 1/4, Sec. 6, T. 42 N., R. 6 W; Yreka Quadrangle, Siskiyou County, California.

Unit	Description	Thickness in feet
	Gazelle Formation, top and bottom not exposed.	
	Payton Ranch Limestone Member	
6	Limestone, finely crystalline, light-gray, very thick-bedded, massive, sparsely fossiliferous; top removed by erosion.	123
5	Shale, calcareous, brown, thinly interbedded with limestone; abundant corals and brachiopods.	11
	Undifferentiated Gazelle Formation	
4	Graywacke, coarse-grained, dark gray, poorly stratified; grains predominantly volcanic rock particles. Contains lenses and angular pebbles of chert. Grades upward into fine-grained sandstone, siltstone and shale.	418
3	Bedded chert, light gray.	25
2	Covered	96
1	Bedded chert, black; base unexposed.	40
	Total	713

III Southeast end of Electro Lime and Chemical Company quarry, NE 1/4, Sec. 8, T. 42 N., R. 6 W., Yreka Quadrangle, Siskiyou County, California.

Unit	Description	Thickness in feet
	Gazelle Formation, top and bottom not exposed.	
	Payton Ranch Limestone Member	
3	Limestone, finely crystalline, light to dark-gray, very thick-bedded, abundant corals and brachiopods; top removed by erosion.	65
2	Shale, calcareous, brown, thinly interbedded with dark-gray limestone; abundant coral and crinoid fragments.	10
	Undifferentiated Gazelle Formation	
1	Conglomerate, dark-gray, pebbles predominantly chert and argillite. Grades upward into sandstone. Base unexposed.	10
	Total	85

The rocks of the Gazelle Formation are characteristically eugeosynclinal in nature. Rapid deposition under conditions of concurrent diastrophism and vulcanism is readily inferred from the lenticular nature of the rocks, the dominance of unstable minerals in the abundant volcanic graywacke, and the presence of indigenous reworked sedimentary materials in the widespread conglomeratic rocks. Unreworked volcanic rock is not abundant, however, in the Gazelle area. The existence of local areas of slower deposition, however, may be inferred from the presence of subordinate amounts of well sorted, relatively pure quartz arenite and oolitic limestone.

The problem of the origin of the Payton Ranch Limestone and the other limestone bodies remains without a definitive solution. Oolitic limestone is known to form in shallow, agitated aerated waters surrounding organic reefs, but may also form on shallow calcareous banks or on beaches. Limestone breccias and conglomerates are also characteristic of reef environments, but these rocks may be formed by submarine slumping on the margin of shallow calcareous banks. Furthermore no field evidence was noted of the activity of frame-building organisms and none of the limestone thin sections indicated origins other than as calcareous mud or as accumulations of fine bioclastic debris. Thus, although it is possible that the limestone of the Gazelle Formation may be of reef origin, it seems more probable that the limestone was deposited on local calcareous banks in areas of slow accumulation.

Metamorphic rocks.—The metamorphic rocks, herein referred to as "phyllite and chlorite-muscovite semischist" and associated rocks, pertain to the Duzel formation of Wells, Walker and Merriam (1959). Phyllite and chlorite-muscovite semischist crop out along the ridge in the northeastern edge of the area and cover the top and eastern slopes of Scarface Ridge in the west. These rocks rest on the Silurian sedimentary rocks to the south and east (figs. 1 and 2).

The phyllite is a fine-grained, pale-green to bluish green schistose rock. Schistosity surfaces have a silky sheen produced by muscovite and chlorite. Two intersecting lineations are well developed in the phyllite of which the first-formed is apparently produced by the intersection of shear surfaces and bedding. Subsequent deformation of the schistose surfaces into small parallel corrugations with amplitudes as small as a few millimeters is responsible for the

stronger, later-formed lineation. These minute folds in turn are superposed on much larger folds having axes parallel to the major fold axes.

Semischist as defined by Turner (Williams and others, 1955, p. 205) and phyllite are closely related rocks and one grades into the other. The semischist in this area is a hard, pale-green, medium to coarse-grained schistose rock that is intensely crumpled and folded. Sheared, elongate grains and scattered pebbles form a pronounced lineation in the semischist. Minute folds also parallel the lineation of the elongate grains. The rock is chiefly composed of coarse, strained, partially granulated crystals (porphyroclasts) of quartz and albite. These are associated with relic ovoid fragments of chert and volcanic rock in a fine-grained schistose matrix of quartz, feldspar, muscovite, pale-yellowish-green mica, chlorite, leucoxene and sphene. The relic grains of albite have well-developed polysynthetic albite twinning with the twin lamellae disrupted and curved in many grains. Minute shreds of sericite penetrate the albite and patches of calcite and rhombs of dolomite partially replace the rock. Veins of calcite and quartz cut across the schistosity and since these veins are not deformed, they must have developed subsequent to the development of the prominent schistosity.

The phyllite and semischist are the product of low-grade, regional metamorphism, and they indicate the former presence of pelitic and quartzofeldspathic sedimentary rocks respectively. In the semischist the nature of the parent rock is recognizable because of the mineralogy and texture of numerous undestroyed fragments of chert, albite, quartz, and volcanic rocks. Thus the semischist may well have been derived from volcanic sandstone of the type occurring in the Gazelle Formation below the Payton Ranch Limestone. The phyllite appears to be derived from shale. No fossils were found in the metamorphic rocks, and therefore their age is conjectural. Thus they may be either older or younger than the Gazelle Formation.

Intrusive rocks.—A large serpentinized pyroxenite-peridotite pluton intrudes Paleozoic rocks in the southeastern part of the area. This ultrabasic rock is altered to dark green serpentinite, characterized by a bastitic structure of serpentine pseudomorphs after original orthopyroxenes. Contacts between the serpentinite and adjacent sedimentary rocks are steep and lack evidence of pronounced contact metamorphism. This absence of baking and contact metamorphism of the host rock suggests that the temperature of intrusion of the pluton was of the order of a few hundred degrees or less. The preservation of bastitic structure, presumed to form under static conditions, implies that serpentinization was incomplete at the time of intrusion.

A few small isolated dikes of serpentinite penetrate the Paleozoic sedimentary sequence north of the ultrabasic pluton. These rocks are composed of green, flaky, antigorite serpentine and are strongly sheared. Thus they probably developed under stress along faults and fractures in the sedimentary rocks.

Small bodies and dikes of hornblende quartz diorite and hornblende diorite intrude both the sedimentary and metamorphic rocks. The sedimentary rocks are baked along contacts with these medium-grained intrusive rocks, but the absence of new mineral assemblages around the intrusions indicates that

the magma was relatively "dry." These intrusive bodies dip steeply and their trend is generally north-south.

Extrusive rocks.—Several discontinuous bodies of Tertiary and/or Quaternary basalt crop out in the area. The largest of these is on the crest of a high ridge in the northeast part of the area. Here olivine basalt unconformably overlies phyllite. This body is layered, and apparently includes several individual flows. In thin sections abundant fresh phenocrysts of olivine can be seen in a matrix of calcic plagioclase laths, subhedral augite and magnetite.

The other two basalt outcrops lie close to the valley floor near Lime Gulch Road. The northernmost outcrop at the south base of Bonnet Rock is a highly altered basalt composed essentially of microlites of plagioclase in a black, iron-rich, glassy groundmass. Fibrous aggregates of actinolite fill amygdules and abundant minute scales of hematite with some specks of magnetite occur in the groundmass. The other body crops out just south of Lime Gulch Road. This mass is an andesite-basalt, consisting of andesine laths subophitically intergrown with augite, both of which are altered in part to chlorite. A few euhedral crystals of almost completely chloritized olivine occur in the groundmass and accessory grains of ilmenite partially altered to leucoxene are disseminated through the rock.

Differences in mineral composition, texture, and degree of alteration suggest that these basaltic rocks west of Gazelle may represent several separate flows. The floor of Shasta Valley just east of the area contains great quantities of volcanic material. This rock belongs to the Tertiary Western Cascade series and the younger High Cascade series produced in late Tertiary to recent time. Evidence in the Gazelle area, however, is inadequate to correlate the local basalt flows with those of Shasta Valley, though close proximity suggests they are related to the same volcanic activity.

PALEONTOLOGY OF THE GAZELLE FORMATION

Fossils, chiefly brachiopods and trilobites, are widespread in thin-bedded limestone interbedded with shale at the base of the Payton Ranch Limestone Member and other limestone bodies in the Gazelle formation. Isolated brachiopods, corals and stromatoporoids also are scattered through the massive limestone, but only unidentifiable fossil fragments were noted in the graywacke, shale and bedded chert. Very few fossils occur in the conglomerate and these are within limestone pebbles and boulders.

The following organisms have been identified in our collections from the Gazelle Formation and are listed below with the known ranges of the genera to which they belong:

Trilobita

Dicranopeltoides cf. *D. decipiens* (Weller)—M. Ord.: Siberia, U. Ord.—Sil.: Europe, M. Sil. (?): eastern North America.

Cheirurus cf. *C. insignis* Beyrich—U. Ord.—Sil.: Bohemia, M. Sil.: eastern North America.

Encrinurus (*Cromus*) *beaumonti* (Barrande)—Ord.—Sil.: Europe, North America and Alaska.

Leonaspis (*Acanthalomina*) *minuta* (Barrande) (=*Odontopleura* in part of American authors)—L. Sil.—U. Dev.: Europe. L. Sil.: Siberia. Ord.—Sil.: eastern North America.

Proetus sp. indet.—M. Ord.—U. Dev.: cosmopolitan.

Scutellum sp. indet.—Ord.—Dev.: Europe and North America.

Trochurus sp. indet.—U. Ord.—Dev.: Europe. Sil.: eastern North America.

Brachiopoda

Leptaena rhomboidalis Wilckens ?—Sil.—Dev.: cosmopolitan.

Atrypa reticularis Linnaeus var. *orbicularis* Sowerby ?—M. Sil.—L. Miss.: cosmopolitan.

Atrypella scheii (Holtedahl) ?—M. Sil.—U. Sil.: Europe, Asia, North America, Ellesmereland, Alaska.

Gypidula sp.—Sil.—Dev.: Europe and North America. Dev.: China, Russia and Morocco.

These data clearly indicate that the fossiliferous portion of the Gazelle Formation is Silurian and that it is probably Middle or Upper Silurian. Closer correlation, however, must be dependent upon further collection in the Gazelle Formation and upon more extensive and detailed descriptions of other Silurian fossil assemblages from western North America. At present these faunas are very poorly known and the isolated Gazelle assemblage must be compared directly with fossils from the standard sections of eastern North America, England, Bohemia and Siberia. Such comparisons are useful in the study of intercontinental faunal distributions, but may give an exaggerated cosmopolitan appearance which obscures the indigenous character of the region's fauna. Experience shows that when fossils previously considered conspecific with animals from eastern North America and Europe, are directly compared with the type specimens, it becomes apparent that separate species occur in western North America. These western species, however, are generally closely related to their counterparts in Europe and eastern North America and it may be inferred that they have approximately the same time-stratigraphic range. Fortunately the trilobite and brachiopod genera so-far identified in the Gazelle fauna are widely distributed and many have been considered excellent index fossils for long-range correlation. Thus although general correlation is secure, it is not practicable to make critical comparisons at the specific level without access to good comparative collections.

The trilobite fauna of the Gazelle Formation includes several new records for western North America. *Dicranopeltoides*, *Trochurus*, *Cheirurus*, *Acanthalomina* and *Scutellum* are all previously unreported from the western states, although they are known to occur in eastern and middle-western North America. Tentative comparisons on the specific level, however, clearly indicate that the Gazelle trilobites are more closely related to Middle and Upper Silurian faunas of Asia and Bohemia than to those of eastern North America. In addition the brachiopods seem more closely related to those of Alaska and Asia than to those of interior and eastern North America. Thus the faunal aspect of the Gazelle Formation is in harmony with the conclusion of C. W. Merriam (personal communication) that the Lower Paleozoic faunas of northern Cali-

fornia are distinctly different from those of the Great Basin and have their closest affinities with Alaskan and Asian assemblages.

GEOLOGIC STRUCTURE

The largest and most striking structural feature of the area is a folded thrust fault which brings the metamorphic rocks on the north and west into contact with the Gazelle Formation (fig. 1). Phyllite and semischist cap the highest peaks and ridge tops along the northern and western borders of the area and were observed to crop out several miles north of the mapped area. Much of the contact between the sedimentary and metamorphic rocks is concealed by rock debris and thick vegetative cover and there are no clear-cut exposures of the fault-plane. At numerous points along the ridge extending north from Mallethead Rock and on the ridge northwest of the prominent limestone outcrops in upper part of the North Branch of Willow Creek, however, beds of sandstone beneath the metamorphic rocks are sharply truncated at the contact. At Mallethead Rock, one of the localities where the metamorphic-sedimentary rock contact is exposed, beds of limestone, sandstone and chert are steeply dipping and slightly overturned beneath the metamorphic rocks (fig. 4). Here

Fig. 4. View northwest toward Mallethead Rock. Hill on right is capped by semischist. Steeply dipping to overturned beds of chert, sandstone and limestone form the saddle and the double-crested hill (Mallethead Rock) in the center of the photograph. The Mallethead Thrust crops out at the foot of the slope on the right-hand side of the saddle and the fault-plane of a subsidiary fault is exposed in the overhang beneath the right-hand limestone mass in Mallethead Rock.

and elsewhere, sedimentary rocks directly beneath the metamorphic rocks are strongly crumpled, sheared and brecciated. These strongly deformed rocks, however, occur only in a thin zone near the contact. Several samples of sand-

stone, taken less than 50 feet below the contact, show no schistosity, lineation, or granulation of grains. Also only minor chloritic and sericitic replacement occur in these rocks. In fact, all of the quartz arenite and graywacke below the metamorphic rock and the sheared zone lack cataclastic texture and contain far less muscovite, sericite and chlorite than does the semischist. On the other hand, the phyllite and semischist clearly have been altered by cataclastic deformation aided to a lesser degree by purely chemical processes. Thus it appears that the sedimentary rocks were not subjected to the same metamorphic environment that produced the phyllite and semischist. This, in turn, means that the metamorphic rocks could not have been metamorphosed in their present position without the process also resulting in alteration of the Gazelle Formation. Thrust faulting offers a suitable mechanism to explain their present close juxtaposition in which metamorphic rocks cap the ridges and hills and sedimentary rocks crop out in the valleys and on the lower hill-slopes. Furthermore the areal distribution of the metamorphic rocks, their stratigraphic position, and the nature of the sedimentary-metamorphic contact, indicate that allochthonous metamorphic rocks have been thrust over the Paleozoic sedimentary rocks. This fault is named the Mallethead thrust fault because of its good exposure at Mallethead Rock.

Evidently the initial dip of the thrust plane was low, but folding subsequent to thrusting has produced dips as high as 30°. A broad anticlinal fold in the thrust plane plunges northward from Bonnet Rock. Here erosion has removed the metamorphic rocks of the overthrust block and Gazelle Formation is exposed along the axis of the plunging fold as far north as Stoner Gulch. In addition the outcrop pattern of the thrust suggests the presence of a second large anticline roughly parallel to the first but with the axis lying west of Mallethead Rock and Scarface Ridge.

Information from the Gazelle area, shows that movement along the Mallethead Fault must have been at least as great as four to five miles. Regional relationships suggest but do not require that the overthrust block came from the northwest. Additional mapping to the north and west, however, is required to ascertain the regional extent of the fault and may permit more accurate determination of the direction and amount of movement. Thus although the Mallethead Thrust may be a major structural feature of regional significance, it also may be merely a local feature along the front of a progressively metamorphosed terrain.

Structural patterns within the phyllite and semischist are exceedingly complex and have not been thoroughly investigated. It is apparent, however, that the numerous wrinkles, minor folds and faults which deform the foliation planes of the metamorphic rocks have no counterpart within the mass of the Gazelle Formation.

Two large anticlines with superposed smaller folds are developed within the Gazelle Formation. These extend from the divide between the Middle and North Branches of Willow Creek to Stoner Gulch and their axes parallel the axes of the folds in the thrust plane. Axes of most of the folds in this system trend N. 20° W. to N. 30° E. and plunge less than 20° N. The absence of traceable structural horizons in the valley of the Middle Branch of Willow

Creek prevents ready recognition of fold axes, but the attitudes here generally suggest a similar pattern of folding.

A series of high-angle, longitudinal faults have broken the two major anticlines and their intervening syncline in the valley of the North Branch of Willow Creek. The strike of these faults trends approximately north, roughly parallel to the fold axes. Most are normal faults, but a few show evidence of strike-slip movement. At least two transverse faults of small displacement trend northwest and many additional minor faults locally offset the Payton Ranch Limestone. These, however, cannot be traced with assurance in the highly fractured detrital rocks beneath. Similar faulting doubtless affects the rocks in the valley of the Middle Branch of Willow Creek, but lack of traceable key horizons again largely frustrates structural mapping in this area.

Slaty cleavage is developed in shale and siltstone throughout the Gazelle Formation. Cleavage attitudes are more or less parallel to the axial planes of the folds and are generally vertical. In many places the bedding of the Payton Ranch Limestone is discordant with that of the shale and sandstone beneath. Here beds of shale and sandstone are crumpled and sheared in contrast to brecciation and slickensiding in the limestone. Evidently local faulting between the limestone and less competent shale occurred at the time of regional folding.

GEOLOGIC HISTORY

The metamorphic rocks above the Mallethead Thrust record deposition of sedimentary rocks rich in volcanic material adjacent to the Gazelle region. Subsequently these rocks were altered to semischist and phyllite under conditions of regional metamorphism. These rocks, although they may be younger than Silurian, are confined to the overthrust block and are tentatively considered of pre-Silurian age.

In the Gazelle area, a thick sequence of volcanic graywacke, bedded chert, conglomerate, shale and limestone record deposition in a tectonically active environment. The fossils of the Gazelle Formation show that much, if not all, of this deposition took place before the end of the Silurian period. Thereafter, the phyllite and schist were thrustfaulted into the Gazelle area. Structures within the Gazelle Formation which are truncated by the thrust plane may have been formed during this orogeny or may be older.

Regional mapping in the Klamath Mountains (Diller, 1906) has established that the major period of igneous intrusion and deformation occurred at approximately the same time as the injection of the Sierran batholiths. Diller (1906) is of the opinion that this took place during the Jurassic or early Cretaceous, and Hinds (1934) concludes that the Shasta Bally batholith, the main intrusion in the Klamath Mountains, is of Late Jurassic age. Later work with radioactive age dating methods, however, suggests that the Sierran and Klamath granitic intrusions are more likely to be early Late Cretaceous (Larsen, E. S. and others, 1958). Thus it is inferred that the large ultrabasic pluton and the smaller diorite and quartz diorite bodies in the Gazelle area were intruded during the late Jurassic or Cretaceous, and most probably during the early Late Cretaceous. There is, however, no evidence within the area to support precise age assignments for these events.

Folding of the thrust plane probably occurred in association with intrusion of the igneous bodies, but may have accompanied uplift and erosion of the area. Late Cretaceous rocks near Yreka overlap the older rocks and are a record of subsidence and marine deposition subsequent to the so-called Nevadan orogeny in this area. Deposition of these rocks was followed by uplift and erosion prior to extrusion of the Cenozoic lavas.

Thus the gelogic history of the Gazelle region is a complex of repeated cycles of marine deposition, vulcanism and orogeny. There is evidence suggesting at least one pre-Silurian orogeny and clear evidence of two periods of deformation between the beginning of the Silurian and before Tertiary time. In addition vulcanism has been active in the area in both Silurian and Cenozoic time. Evidence suggestive of additional orogenic cycles is also present, but further detailed study in adjacent areas is required to verify this hypothesis.

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A PETROFABRIC ANALYSIS OF A FOLD

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ABSTRACT. A petrofabric method whereby polygenetic folds can be analyzed is described. The method has been applied to the study of the tectonic history of a fold from the Grampian Highlands of Scotland. An earlier deformation was produced by shearing, followed by accordion folding, utilizing the same S-planes.

SUMMARY OF PREVIOUS WORK

Detailed analyses of folds have been made by various workers, following the classic description by Sander (1930) of a folded quartzite from Brenner, Tyrol. This fold was a flexure fold, and similar structures have been described by Turner (1948), Ingerson (1940), and others.

Ladurner (1954) described a method by which a polygenetic fold (in this case shear, followed by flexure) could be analyzed, and also described the analysis of such a fold. Jones (1959) first described the method in English, and also attempted the analysis of polygenetic folds, but came to the conclusion that possibly later movements had obliterated the earlier fabric.

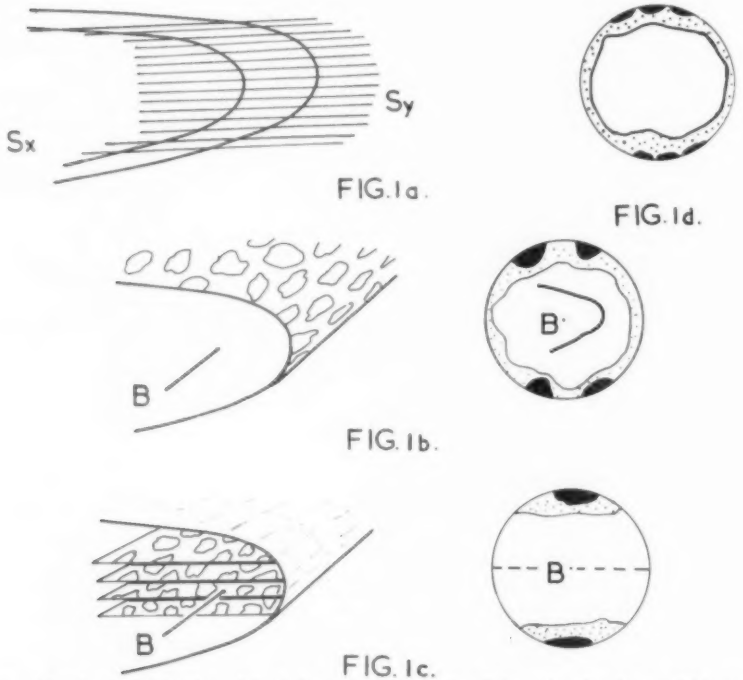

Fig. 1. (a) Relation of S_x & S_y to fold, (b) Mica Orientation for flexure fold, (c) Mica Orientation for shear fold, (d) collective mica diagram.

MONOGENETIC FOLDS

Folds of this type may originate through (a) pure shear, (b) pure flexure, (c) flow, and, (d) any combination of these processes.

The common orientation rule for micas is that in which the (001) cleavage plane lies in an S-plane, with the "c" crystallographic axis normal to the S-plane. The orientation of the quartz will be considered subsequently.

(a) *Fold formed by pure shear.*—The fold is formed by deformation along an infinite or finite number of shear planes (S_y), usually parallel to the axial plane of the fold (fig. 1a). The micas will become oriented, either by syntectonic crystallization or by subsequent growth along S-planes. They will be oriented, firstly, by deformation of the original S-plane (S_x), and will produce a girdle developed about the fold axis as axis of symmetry, with maxima corresponding to the limbs (fig. 1b and Ingerson, 1940). Secondly they will be

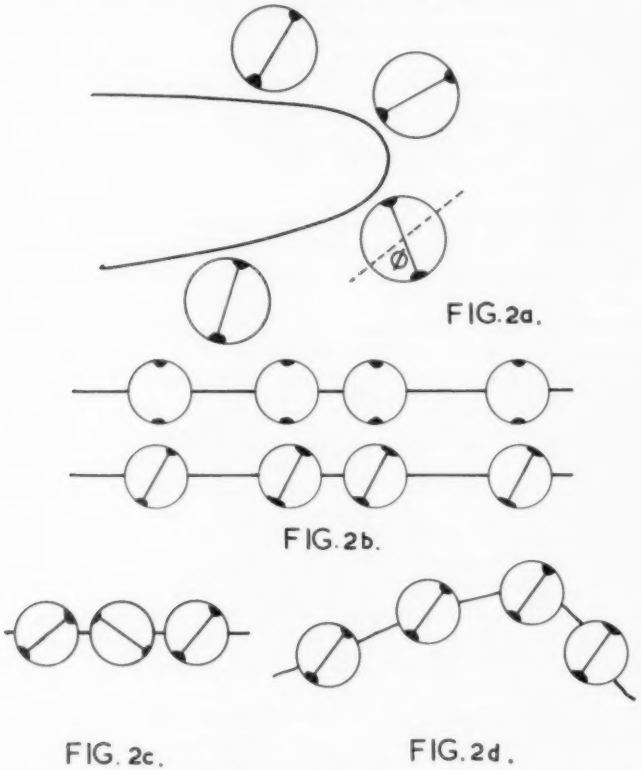

Fig. 2. (a) Relation of q-richtungen to fold, (b) Parallel alignment of q-richtungen on unfolding 2a. Mica diagram, above; Quartz diagrams below. (c) Relation of q-richtungen on complete unrolling of a polygenetic fold. (d) Polygenetic fold partly unfolded so that q-richtungen are parallel.

oriented parallel to the shear planes (S_y) in the fold, giving a preferred orientation of the "c" axes perpendicular to the shear direction (fig. 1c). In practice, however, it will be found difficult or impossible to distinguish between the two types of micas, and the fabric diagrams will be superimposed (fig. 1d).

The fabric of the quartz grains will be identical in all parts of the fold, no matter which orientation rule the quartz follows, and the main sets of maxima will be in the same relative positions (Ladurner, 1954).

(b) *Fold formed by pure flexure.*—The fold is formed by pure flexure, or flexural slip, whereby the fold develops by rotation about the axis (B) with attendant slip upon the primary S-plane (S_x), in order to accommodate the core without rupture. In this case the mica orientation will form a girdle about "B", with maxima corresponding to the limbs (fig. 1b).

Provided that the quartz grains in the fold had an originally anisotropic fabric, then the quartz orientation diagrams, at all points on the fold, will each have an identical relationship with the tangent to the fold. For example, assuming that the initial quartz orientation was such that it made an angle of $\phi°$ with S_x in the plane of section, then as S_x is folded about "B", the relationship of the quartz axes to the fold will appear as in figure 2a. The S-planes, as defined by the mica maxima, can then be brought into alignment and the fold "unrolled", with the q-richtungen[1] for the quartz diagrams lying parallel to each other (fig. 2b).

(c) *Fold formed by flow.*—The fold is formed by flow, in which there is no relation between the planes of deformation and the stress direction. The quartz fabric will tend to be markedly heterogeneous, and the symmetry of the fabric will not correspond to the symmetry of the fold. The layers in the fold will become stretched and thickened, and it will be impossible to estimate the shortening involved (Hills, 1951; De Sitter, 1956).

POLYGENETIC FOLDS

This group includes folds which have been formed, or modified, by one type of deformation followed by another (e.g. shear followed by flexure, or vice versa).

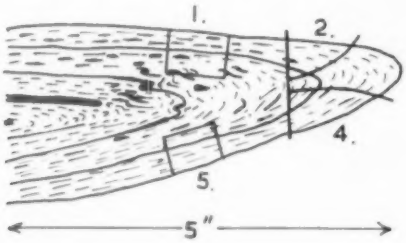

FIG. 3

Fig. 3. Diagram of fold showing position of sectors. The sections were cut normal to the fold axis (120°N).

[1] q-richtungen are lines joining maxima to the center of projection (Ladurner, 1954).

Shear followed by flexure.—Such a structure may be defined by referring to the description of the folds analyzed by Ladurner (1954) and Jones (1959).

Ladurner, on completely "unrolling" a fold, found that the angle ϕ was not the same for each sector (fig. 2c). He overcame this difficulty by *partially* unfolding the fold until the q-richtungen were aligned parallel to each other (fig. 2d). The fold was thus initiated by shear, to give the shallow fold in figure 2d, and the fold was subsequently tightened by flexure of S. In the fold discussed by Ladurner $\phi = 68\text{-}78°$, and it retained its original fabric axis and a-c symmetry plane.

Flexure followed by shear.—With this type of deformation, the analysis is more complex. There will be an original mineral orientation, related to the folded S-plane (S_x), upon which is superimposed an orientation induced by shearing. It is possible that this later shear will completely obliterate the fabric of the earlier flexure. Where there are more than two modes of deformation, it will probably be impossible to detect the first unlss the later dformations have been much less intense.

APPLICATION TO A FOLD

In order to illustrate these principles an analysis of a fold from the Grampian Highlands of Scotland will be described (see fig. 3). The fold was located 2¾ miles west of Balquhidder (British Nat. Grid. Ref. NN/490207). The reversal of direction of curvature in small quartz veins in the core of the fold indicates that a certain amount of flexure has occurred during the evolution of the fold (Sander, 1930; Turner, 1948). The fold was divided up into a number of segments, the nose of the fold being subdivided into as many sectors as possible (fig. 3).

The sectors 1 and 5 give mica diagrams which can be related to the primary S-plane (S_x) (fig. 4). Sectors 2 and 4 give orientation patterns which define a statistical S-plane sub-parallel to the axial plane of the fold (S_y). Sector 3 gives a more complete girdle, with maxima that can be related to S_y and the limbs of the fold (see also fig. 1d). The mica diagrams in the nose of the fold define slightly divergent S-planes (fig. 7c).

On the basis of the mica fabric, the limbs of the fold have been affected by flexural slip, the nose and the region bordering the axial plane having been affected by shear acting parallel or sub-parallel to the axial plane of the fold. The relation of the q-richtungen to the quartz diagrams and the diagrams to the fold are shown in figure 6b, the pattern of the q-richtungen being similar in each case. In sector 2 the q-richtungen that can be drawn are greater in number, but directions can be found which correspond to the pattern constructed for other diagrams. The fabric diagrams for the nose of the fold give, in general, much sharper and more clearly defined orientation patterns than on the limbs. The patterns are identical in the sectors 1 and 5, but one diagram is the mirror image of the other. Use could not be made of the mica diagrams in unrolling the fold (Ladurner, 1954), but only of tangents to the S_x plane which could be determined in the hand specimen.

In the completely unfolded state, the quartz diagrams will be related as in figure 7a. The measure of the flexure of the fold can now be obtained by

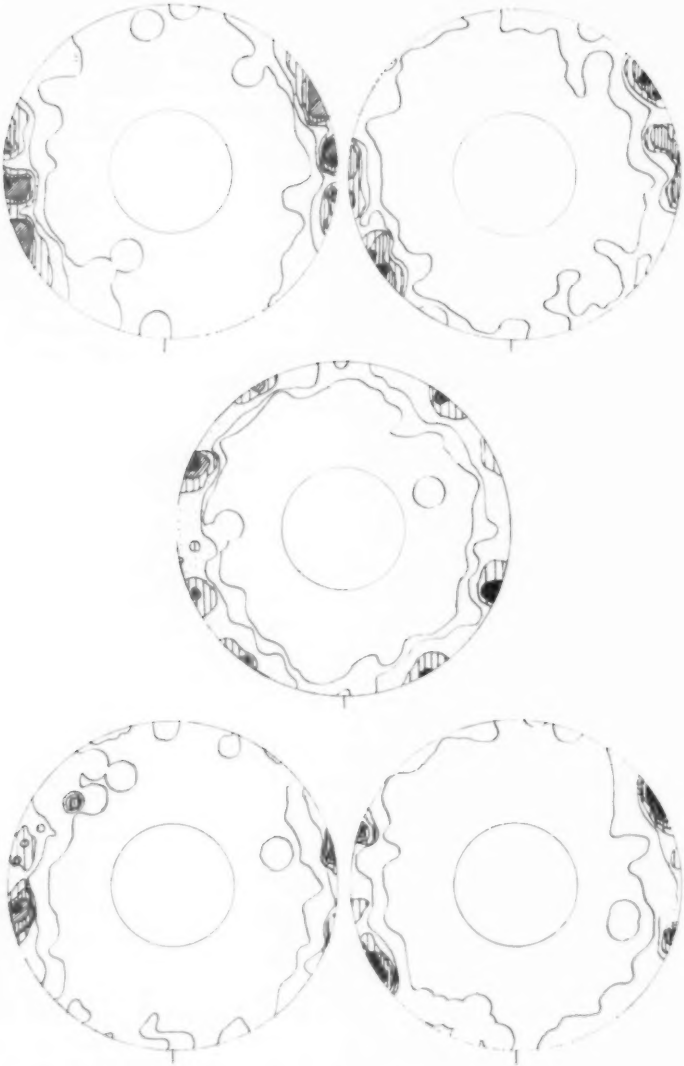

Fig. 4. Mica & Chlorite diagrams, poles to (001) cleavage.

Sector 1: 100 micas; contours at 15, 12, 10, 8, 5, 1% per 1% area.
Sector 2: 105 micas; contours at 12.6, 10.5, 7.3, 5.7, 3.6, 0.91% per 1% area.
Sector 3: 130 micas; contours at 10, 8, 6.1, 4.6, 2.4, 0.8% per 1% area.
Sector 4: 100 micas; contours at 12, 10, 8, 6, 4, 1% per 1% area.
Sector 5: 100 micas; contours at 16, 12, 10, 8, 5, 1% per 1% area.

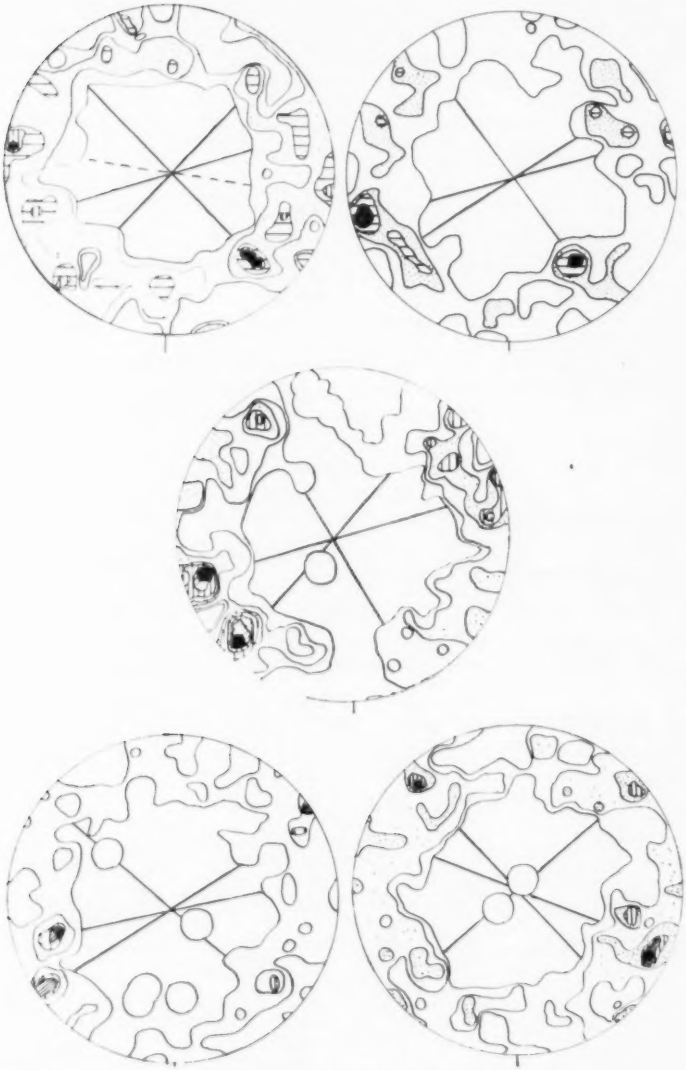

Fig. 5. "c" axes diagrams of small rounded quartz grains.
Sector 1: 110 grains; contours at 7.4, 5.5, 4.5, 2.7, 0.9% per 1% area.
Sector 2: 150 grains; contours at 4.7, 4, 2.7, 1.3, 0.7% per 1% area.
Sector 3: 154 grains; contours at 5.3, 4, 2.7, 1.3, 0.7% per 1% area.
Sector 4: 136 grains; contours at 5.6, 5, 3.6, 2.1, 0.7% per 1% area.
Sector 5: 154 grains; contours at 5.3, 4.7, 4, 2.8, 1.3, 0.7% per 1% area.

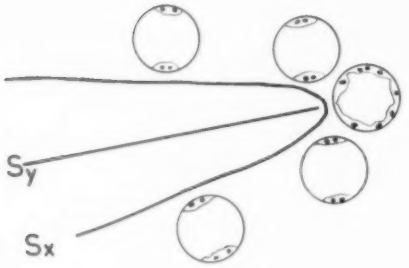

FIG.6a

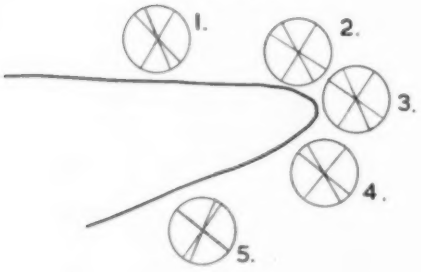

FIG.6b

Fig. 6. (a) Idealized relationship of mica diagrams to the fold.
(b) Relationship of q-richtungen to the fold.

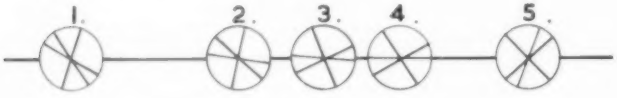

FIG. 7a.

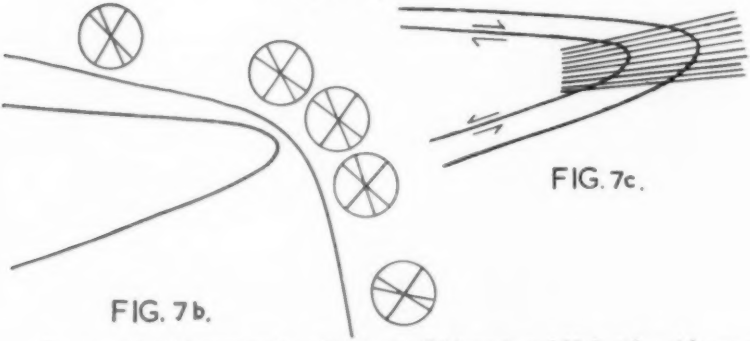

FIG. 7c.

FIG. 7b.

Fig. 7. (a) Fold completely unfolded. (b) Fold partly unfolded with q-richtungen patern roughly parallel. (c) Accordion folding.

unfolding the fold so that the q-richtungen lie parallel to each other (fig. 7b). The symmetrical relations of the q-richtungen to the limbs of the fold, indicates that the fabric was impressed upon the rock prior to the later folding (Ladurner, 1954).

The origin of such a structure may therefore be summarized:

(1) Shear folding produced the open fold form in figure 7b, and impressed an appropriate quartz fabric on the rock.

(2) Flexural slip folding with concomitant axial plane shearing (accordion folding) utilized the same shear planes and directions (S_x), resulting in the mica orientation patterns and sharpening the quartz fabric in the core of the fold (fig. 7c).

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RADIOCARBON-DATED ORGANIC SEDIMENT NEAR HERBERT, SASKATCHEWAN

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ABSTRACT. Organic sediments from a depth of 11 feet near Herbert, Saskatchewan, contain willow wood which has been radiocarbon dated at 10,050±300 years B.P. The sediments contain in addition to the wood a faunule of predominantly snails and ostracodes. Plant fragments are common and include a few spruce cones. Marl with abundant remains of algae (*Chara*) is locally present. Spores and pollen recovered from the sediment provide an insight into the type of vegetation at the Herbert site, 10,000 years ago.

Fauna and flora indicate sedimentation in quiet water of a pond or small lake in a spruce-pine parkland with a few northern, broadleaved trees such as birch, willows, and probably aspen. Such an environment exists today in the forest belt of Saskatchewan, 200 miles to the north of Herbert. The change from forest to glassland, which now prevails near Herbert, is indicated by pollen analyses of the sediments overlying the radiocarbon dated wood.

INTRODUCTION

In August, 1940 Mr. J. H. Giesbrecht of Herbert, Saskatchewan, submitted to the Saskatchewan Museum of Natural History some samples of peat and several fragments of wood discovered by him at a depth of 11 feet while digging a well about 3 miles south of Herbert. A preliminary investigation of this material was undertaken by Mr. Edgar Houldsworth of Regina, Saskatchewan. A manuscript notebook of Mr. Houldsworth (deceased) is on file in the Saskatchewan Museum at Regina. The locality from where the samples were obtained will be referred to as the Herbert Site.

An excavation, 20 feet north of the well dug by Mr. Giesbrecht, was undertaken under sponsorship of the Saskatchewan Department of Mineral Resources and the Saskatchewan Research Council during the summer of 1956 to obtain wood for radiocarbon dating. This excavation, which was directed by E. A. Christiansen of the Saskatchewan Research Council and the writer, yielded pollen, plant fragments, mollusks, and ostracodes in addition to several pounds of wood. Samples were submitted to specialists for identification. Acknowledgments to these specialists will be made in this paper when discussing the results of their findings. The writer assumed the task of assembling, coordinating, and recording the results of the various investigations.

Herbert, Saskatchewan, is about 114 miles west of Regina. The excavation is about 1,000 feet south of the northeast corner of Section 30, Township 16, Range 9, West of the Third Meridian. It is on the east shore of a small saline lake around which the road bends that leads south from Herbert. The intersection of this road with the Trans Canada or No. 1 highway at Herbert is about 3.2 miles north of the location. The altitude of the site, as determined from the topographic map (Swift Current sectional sheet), is approximately 2,340 feet.

The organic sediments near Herbert are of interest because they provide some insight into the flora and fauna 10,000 years ago in a part of Western Canada of which the early postglacial history was unknown until this time.

GEOLOGICAL SETTING

The town of Herbert is on the bottom of former Lake Herbert of which a

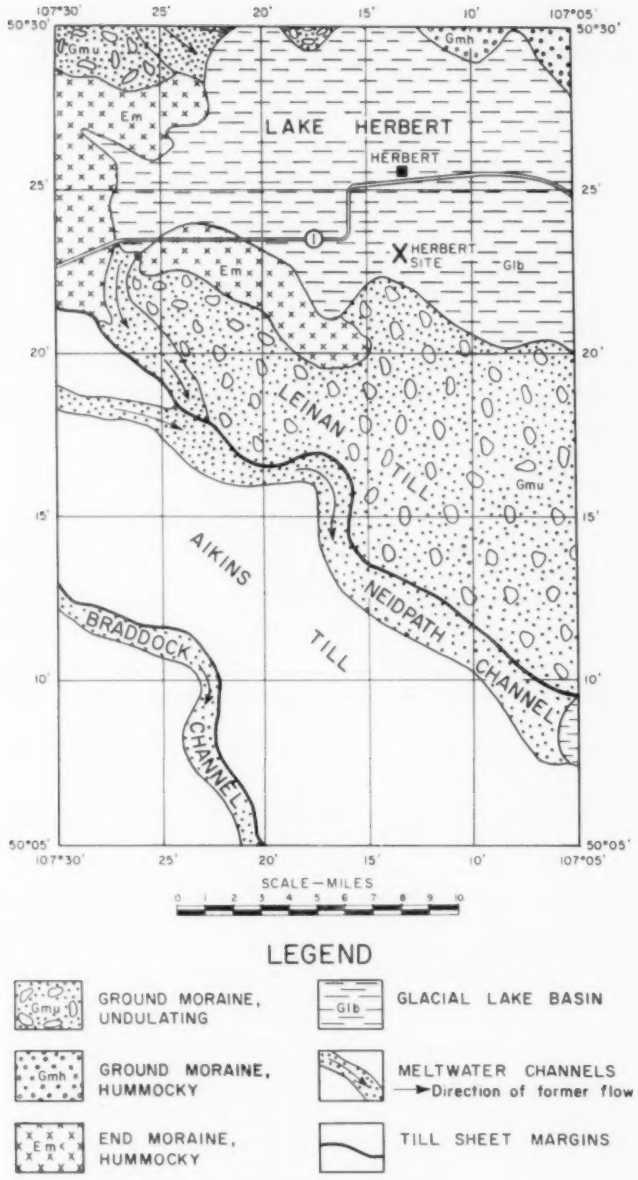

Fig. 1. Geological map (after Christiansen, 1959). Location of Herbert Site added.

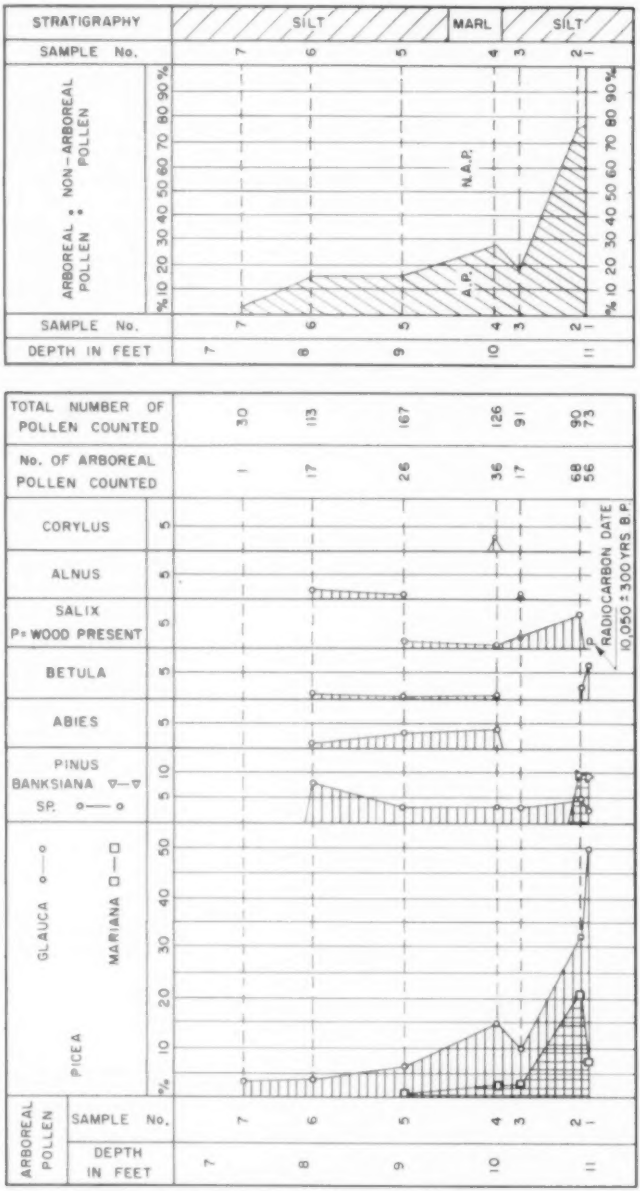

Fig. 2A. Diagram of arboreal pollen and ratio of arboreal over non-arboreal pollen. All percentages are based on the total pollen. Identifications by J. Terasmae, Geological Survey of Canada.

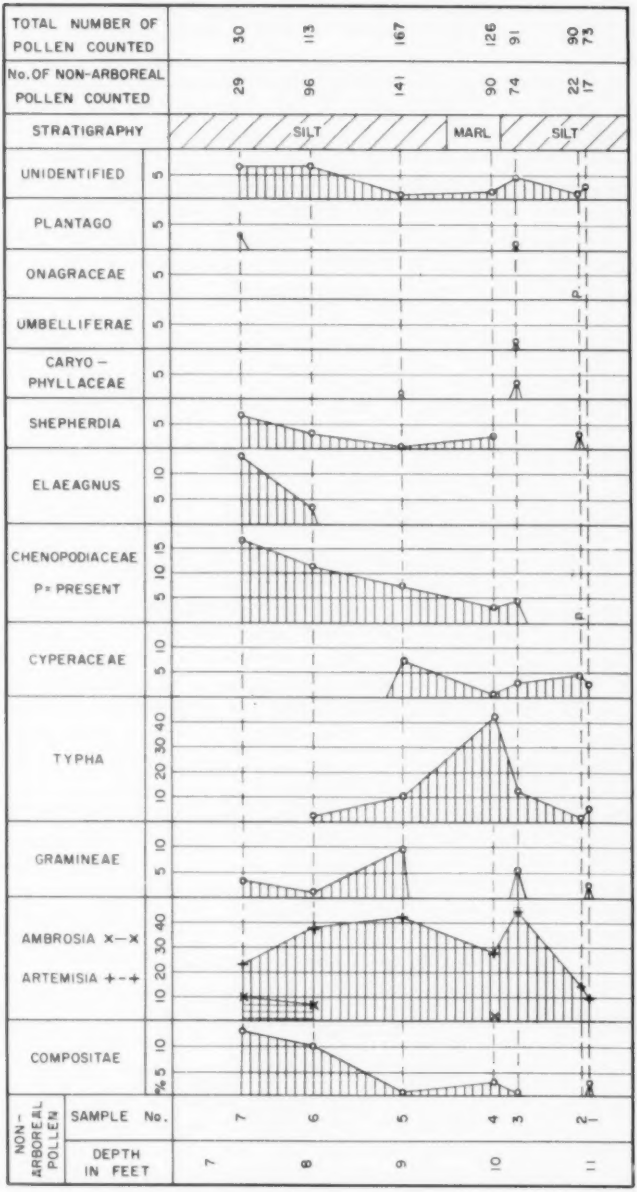

Fig. 2B. Diagram of non-arboreal pollen. All percentages are based on the total pollen. Identifications by J. Terasmae, Geological Survey of Canada.

remnant still exists to the east-southeast of the town. This lake was bordered on the south and west by the northwesterly trending Leinan Moraine (Christiansen, 1959).

The Herbert Site is on the southern shore of the former Lake Herbert, against the undulating to gently rolling Leinan moraine (fig. 1). The highest level of Lake Herbert was at about 2,400 feet, and during the early phases of the lake the Herbert Site was part of Lake Herbert. Later the Herbert Site became a separate pond or small lake, as it is still today, when Lake Herbert drained to the west and south through the Neidpath Channel. The importance of glacial drainage channels in Western Canada as routes for plant migrations in postglacial times has been pointed out by Boivin (1953).

STRATIGRAPHY

The description of the sediments at the Herbert Site is based on information obtained from a hole dug by hand in 1956 to a depth of 12 feet and from core drilling during the summer of the following year, and in 1959. The lithology and sequence of strata below 12 feet is insufficiently known because of poor core recovery.

The deposits are all stratified and no till was observed overlying the sediments. Till can be seen, however, close to the site and it was encountered in one bore-hole at a depth of 55 feet. Silts and very fine grained sands compose nearly the complete section. The upper 23 feet contain varying amounts of organic material which appears to be absent in the lower part of the stratified deposits as determined in several bore-holes. The content of organic material in the upper sediment is in places high enough to warrant the term "gyttja" for some of the dark clayey layers. Partly decomposed plant fragments locally are abundant enough to be called peat. This is especially true for the 10-12 foot depth at the place where the wood was first encountered. Some of this peat found by Mr. Giesbrecht is now on display in the Saskatchewan Museum of Natural History, Regina. Deposits with such a high percentage of recognizable plant fragments were not recovered during the 1956 excavation. The peat appears to grade laterally into mineral sediments with less organic material. The deposits are therefore likely to be variable horizontally as well as vertically. The following abbreviated section thus provides only a generalized description and local variations are to be expected.

Depth interval in feet		Description
from	to	
0	1.5	Soil, clay loam.
1.5	7	Silt, clayey, grading into very fine sand in places, occasional coarse sand grains, light grey to yellowish brown, oxidized, calcareous, laminated. Organic material is not abundant, but finely divided plant detritus is present, as are ostracodes. No spores and pollen recovered. Some iron oxide staining in places forms incipient concretions.
7	9.5	Silt, similar to interval 1.5-7 feet, but with more shell fragments. Pollen and spores recovered. Samples 5, 6 and 7 of palynological analysis (fig. 2).

9.5	10	Marl, light yellowish grey (cream colored), highly calcareous with low mineral content, very finely laminated. *Chara* stem fragments abundant, *Chara* oogonia present. Gastropod shells and fragments abundant in places; some black plant fragments parallel to laminations; roots perpendicular to laminations abundant and well preserved. Thickness of unit variable; unit absent in places. Water table reached at about 10 feet. Sample 4 of palynological analysis (fig. 2).
10	12	Silt, light grey when dry, unoxidized, calcareous, well sorted, laminated with some black laminae. Gradations to very fine sand. Organic material in well defined layers. Where high content of shells and shell fragments the sediment is light yellowish grey (cream colored). Organic material includes *Chara* stem fragments and oogonia. Pollen and spores recovered. Samples 1, 2, and 3 of palynological analysis (fig. 2). The samples used for study of the ostracodes and mollusks were obtained from this unit as well as the willow wood used for radiocarbon dating (S-41), from a depth of 11 feet. The wood appears to have been transported and occurs in fragments parallel to the bedding. Some dark brown to black tubular soft plant fragments perpendicular to the bedding apparently belong to water-rooted plants.
12	13	Pebble zone, suggested by pebbles in drilling mud and loss of circulation.
13	19	Sand, gray, unoxidized, fine grained, argillaceous, calcareous, poorly stratified; contains plant remains. Recovery of unit in core barrel: 13 inches.
19	23	Sand, yellowish brown, oxidized, fine grained, calcareous, massive. Contains few plant remains with blue grey reduced area surrounding specks of organic matter. Recovery: 17 inches.
23	55	Sand, grey, unoxidized (60 percent), calcareous. Organic matter absent. Silt, clayey, greenish gray, calcareous, well sorted, laminated, numerous porous lime concretions ½-1 inch in diameter, visible organic matter absent.
55	58+	Till, dark grayish brown, calcareous.

The above section can be divided into three units: (a) till, below 55 feet, (b) sand and silt without organic matter of glacial or early postglacial age, between 55 and 23 feet, (c) sand, calcareous silt, marl, and gyttja with organic material indicating a postglacial age, above 23 feet.

RADIOCARBON DATING

The wood obtained from the Herbert Site was identified as willow (*Salix* sp.). The woods of poplar (*Populus* sp.) and willow are similar in some respects but a definite determination of the Herbert wood as willow was made by

Dr. J. D. Hale and Mr. E. Perem of the Wood Structure Section of the Forests Products Laboratories of the Canada Department of Northern Affairs and National Resources, Ottawa. An anatomical study undertaken by Mr. J. S. Maini, Department of Plant Ecology, University of Saskatchewan, revealed in addition to the willow wood the presence of Gymnosperm wood, probably coniferous.

The wood consists of fibrous, twisted fragments, several inches long, which disintegrate into smaller curled pieces resembling shavings. Where freshly broken it is dark brown, but the outside is light gray because of the adhering sediment. Bark is not present on the wood. The wood fragments are oriented parallel to the stratification of the enclosing sediment and no roots are present. The wood is therefore not *in situ*, but it does not appear to have been transported over a great distance.

Stem portions of this willow wood were submitted to Dr. K. J. McCallum, Professor of Chemistry at the University of Saskatchewan, for radiocarbon dating. The mean value of two determinations on this sample (S-41) can be given as 10,050±300 years B.P. This value was arrived at by employing the acetylene method and the two determinations obtained were 10,200±300 years and 9,900±350 years.

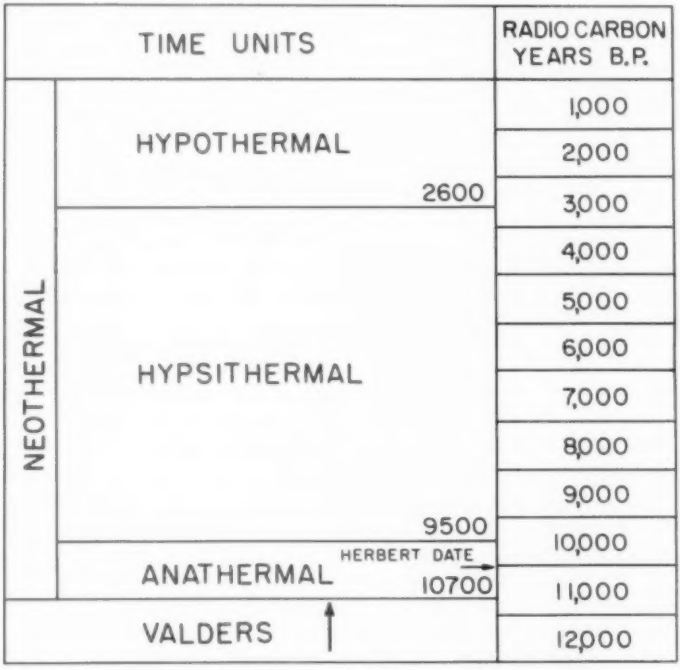

Fig. 3. Time stratigraphic chart (modified after Cooper, 1958).

An age of about 10,050 years for the sediments near Herbert at a depth of 11 feet suggests that these deposits are post-Valders or Anathermal in age if Cooper's (1958) terminology is accepted (fig. 3).

The question where the ice border was at that time can be answered only by reference to the maximum extent of the Valders ice. Two divergent views have been expressed on the position of the maximum extent of the Valders ice, but both suggest that the ice was at least 300 miles away from the Herbert Site. Because the Valders maximum was about 10,700 years ago (fig. 3) the ice had retreated even farther to the north and east at the time of the radiocarbon-dated sediment at Herbert, 10,050 years ago. If the The Pas Moraine is Valders, as suggested by Elson (1957, p. 1000) then the ice stood at least 350 miles away. Lemke and Colton (1958) present a history of deglaciation of North Dakota which suggests that the Valders ice advanced much farther south then assumed by Elson and may have covered northeastern North Dakota as far west as 98°W longitude. If this ice border is projected north into Canada it follows roughly the western boundary of the Glacial Lake Agassiz basin. If this is correct, and if this western margin is traced northward into Saskatchewan, it would mean that the ice was about 300 miles from the Herbert Site at its closest distance during the Valders maximum.

PLANT REMAINS

The willow wood used for radiocarbon dating occurred in a sediment containing abundant plant fragments. These include recognizable fragments of *Chara* stems and some oogonia. A few drupelets of *Potamogeton* (Pondweed) are also present. Houldsworth collected some cones of spruce from a peaty layer at about the 12-foot level, but no more cones were found during the 1956 excavation. He also mentions the presence of stems and fruit of *Lycopodium* (Club-moss), but Mr. K. C. Misra of the Department of Plant Ecology, University of Saskatchewan, could only find leaves belonging to the three distinct species of true mosses (Musci) in the samples submitted to him. Only the moss order Eubrya appears to be represented and the specimens do not contain remains of *Sphagnum* moss.

The plant microfossils (mainly pollen, some spores, and other remains) were investigated by Dr. J. Terasmae of the Geological Survey of Canada. His findings are summarized in figure 2. Samples from various depths were studied, but sample 1 is of most immediate interest as it represents the sediments in which the wood used for radiocarbon dating was enclosed. In reading figure 2 it should be kept in mind that the populations obtained from most samples are small, that the samples are more widely spaced than is desirable for accurate palynological analysis, and that no allowance has been made for over-representation of certain species but that the percentages are recorded as found by Dr. Terasmae.

The data of figure 2 were scrutinized by Dr. Doris Löve, Institut Botanique, Université de Montréal, who states that they are in full accord with her theories regarding postglacial floral migrations into Manitoba and with her contention that the pines are of western origin (Löve, 1959, p. 568).

The plant remains of the 10-12 foot interval of the Herbert Site indicate deposition in quiet water of a pond or small lake, surrounded by an open forest vegetation of black spruce, white spruce, pine, birch, and willow. Aspen (*Populus*) was also likely present. Because pollen of aspen is generally not preserved, its absence in the pollen analysis does not mean that aspen was not a component of the vegetation.

The marl, with its high percentage of cat tail (*Typha*) pollen and its abundance of *Chara* stem fragments, is very similar to that now being deposited in some lakes of central and northern Saskatchewan such as Sturgeon Lake (Kupsch, 1956). The flora surrounding Sturgeon Lake also resembles the vegetation of the Herbert Site 10,000 years ago as is indicated by the tree pollen in the sediments. This flora is typical of the forest belt adjacent to the northern limit of the prairies.

A change from forest conditions, which existed near Herbert 10,000 years ago, to the present prairie vegetation is clearly indicated by pollen-analyses from stratigraphically higher sediments (fig. 2). Especially the abundance of *Artemisia*, *Shepherdia*, *Elaeagnus* and *Chenopodiaceae* as well as the dominance of non-tree pollen in the higher strata is indicative of a tree-less type of vegetation indicating a dry climate, and of the present-day grassland belonging to the *Stipa-Agropyron* community of the Mixed Prairie Association of which the principal broadleaved plants are *Artemisia frigida* and *Phlox hoodii* (Coupland, 1950). This has been the predominant vegetation on developed upland soil in southwestern Saskatchewan since Hypsithermal times (Coupland, personal communication).

Diatoms are present in the sediments from the 11-foot level, but they were not further identified.

OTHER FOSSILS

The silty sediments from which the willow wood was obtained contain many layers with abundant remains of gastropods and ostracodes. Some pelecypods are also present and Houldsworth extracted pupa cases and body segments of unidentified insects and frog bones from the peat.

The Mollusks from the 11-foot level of the Herbert Site were investigated by Dr. A. La Rocque, Ohio State University, who reports the presence of the following species:

PELECYPODA

Pisidium sp. A and *P.* sp. B.

These species are similar to those found in Sturgeon Lake, Saskatchewan (Kupsch, 1957).

GASTROPODA

Lymnaea stagnalis jugularis Say.
Stagnicola palustris (Mueller) var. (? *nuttalliana Lea*)
Helisoma cf. *H. subcrenatum* (Cpr.)
Gyraulus cf. *G. cyclostomus* F. C. Baker
Promenetus exacuous megas (Dall)
Physa cf. *P. gyrina* Say.

The environment indicated by this assemblage is that of quiet, shallow water possibly a small lake or a backwater in a stream. La Rocque (personal communication, 1958) remarks that the absence of *Sphaerium*, *Valvata*, and *Amnicola* indicates an undeveloped fauna, that is, one in which all the species capable of existing in the environment had not yet colonized it. For this reason, the fauna is most likely that of a small lake, an environment reached by mollusks with some difficulty.

Dr. E. M. Winkler, University of Notre Dame, Indiana, studied the ostracod material which he found to be well preserved but without any detectable muscle scar imprints. He determined the following ostracodes:

Cypridopsis dentato-marginata (Daday) cf. *C. parva* (Mueller)

Cypridopsis hartwigi (?) (G. W. Mueller) Bronstein

Cyclocypris forbesi Sharpe 1897

Candona cromagniana Turner 1894

Candona distincta? N. Furtoss 1933

Candona scopulosa N. Furtoss 1933

Candona truncata N. Furtoss 1933

Of the above ostracodes *C. forbesi* is the most common and it can be stated that there is a poverty of ostracod species. Some of the above mentioned ostracodes (*C. dentato-marginata* and *C. hartwigi*) are now living in the arctic and subarctic whereas the others are found in the temperate parts of North America.

ORIGIN OF DEPOSIT

Both fauna and flora obtained from the sediments in the 10-12 foot interval at the Herbert Site indicate a climate that was wetter and also slightly colder than the present. Deposition took place in a small lake with water plants and surrounded by a mixed-wood forest. This environment is similar to that of lakes in the present forest belt of Saskatchewan, about 200 miles to the north of Herbert.

Spruce wood found near Tappan, Kidder County, North Dakota has been radiocarbon dated at 11,480 years±300 years (Moir, 1958). The Herbert deposit verifies Moir's contention that during early postglacial time the region now occupied by prairie was covered by forest vegetation, "not necessarily as a continuous cover but more probably in scattered groupings in the more favorable habitats." The simultaneous occurrence of such "prairie-indicators" as *Artemisia* and *Shepherdia* with the spruce-pine pollen of the 11-foot sample from the Herbert Site suggests that the same was true for southwestern Saskatchewan. The plant community was apparently similar to what can be seen today in the Spruce Woods Forest Reserve, southeast of Brandon, Manitoba, where a spruce parkland surrounded by a prairie upland persisted from about 10,000 B.P. until the present (Löve, 1959, p. 558, 568).

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ICE-PUSHED RIDGES, PERMAFROST AND DRAINAGE

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ABSTRACT. Ice-pushed ridges in regional development are the main glacial characteristics of the northwestern European plain. They were formed during the Riss glaciation and consist of pre-glacial material pushed up into long, straight or curved ridges with an imbricate structure. They developed as a consequence of the formation of a thick permafrost layer in front of the advancing ice sheet.

Ice-pushed ridges of such a regional development are absent from the northern plains of the United States. It is thought that a relative difference in drainage pattern—away from the ice front in the U.S.A. and toward the ice front in Europe—can be held responsible. The presence of ice-pushed ridges in northwestern Canada, where again the drainage is toward the ice front, and their absence in the European Würm glaciation, where outward drainage prevailed, corroborates this theory.

INTRODUCTION

Ice-pushed ridges form a conspicuous feature of the plains of northwestern Europe, stretching in a broad belt with a west-east direction across the middle of Holland and western Germany. Their dimensions are considerable. Their altitude above their surroundings, when counted down to the contemporaneous ground moraines in the adjoining valleys, ranges from 50 m to 200 m. Their linear extent varies from a few tens of kilometers to 100 km for a single ridge.

Ice-pushed ridges (German, *Stauwälle*; Dutch, *Stuwwallen*) are still indicated on many geologic maps as end moraines. But they form entirely different structures. They are built of pre-glacial material, earlier Pleistocene and Tertiary sand, gravel and clay. The material of the ice-pushed ridge formed the pre-glacial surface over which the ice advanced. It was strongly disturbed by the ice, and now dips as much as 50° to 70° over considerable distances. Both strike and dip of these pushed-up and tilted pre-glacial beds remain remarkably constant within an individual ridge. It has been shown (Richter, et al., 1950; De Jong, 1952) that the structure of the ridges consists of long and rather narrow blocks, up to 150 m thick, pushed one on top of each other in an imbricate structure. The strike of the blocks is parallel to the ridge; their dip is away from their outer face of the ridge.

Apart from these pseudotectonics developed through the lateral pushing of the ice, only a thin veneer of drift has been deposited over the ridges. This normally has been washed out strongly, leaving only a sporadic sprinkling of northern erratics on top of the ridges ("reduced ground moraine"). Practically all of the mass of the ridge consists of pushed-up pre-glacial sediments.

Ice-pushed ridges of this size and regional distribution in the northwestern European plain belong to the Riss (= Saale; = Illinoian) glaciation. Of course the outward flow of ice in the big ice sheets has had many other pseudotectonic influences on the subsurface. Woldstedt (1958) cited many instances of local folding, influenced by pre-existing topography. But, because of their size and extent, the ice-pushed ridges here under consideration stand out as a class by themselves. They are characterized by (1) broad regional distribution in the plains; (2) large individual size, both vertical and linear; (3) uniform pattern, with remarkably constant strike and dip; and (4) by their imbricate

structure. The latter is remarkable indeed, because the material is mainly loose sand, gravel and soft clay.

The ice-pushed ridges in Holland have been fully mapped (Pannekoek, 1956, fig. 33). As is schematically indicated on figure 1, they stretch much

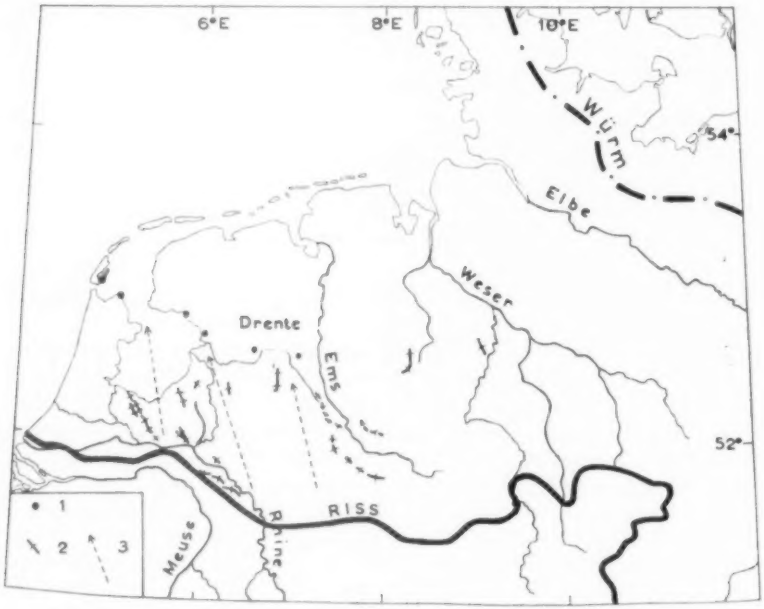

Fig. 1. Map of the plain of northwestern Europe, with the limits of the Riss and the Würm glaciations.

1. Thick till deposits of the end moraines of the Drente stadium of Riss glaciation.
2. Schematic repartition of ice-pushed ridges.
3. Schematic north flowing drainage during Drente stadium of Riss glaciation.

further eastward. Much of what formerly has been called "Endmoränen des Rehberger Stadiums" in reality are not end moraines but ice-pushed ridges. But apart from an area in western Germany (Richter, et al., 1950), no critical detailed studies are known to me.

Their characteristically regular arrangement can be seen in figure 2. The Veluwe, the backbone of the dutch area of ice-pushed ridges, is seen to form a composite ridge. It resulted from the lateral push of various ice lobes advancing southward at slightly different times.

The characteristic imbricate structure of the ice-pushed ridges is seen in cross sections of ridges where two or more distinguishable series of sediments have become incorporated in each thrust-up block. In the northeast of Holland, for instance, only the earlier Pleistocene is involved (De Jong, 1952, 1954;

Pannekoek, 1956, figs. 34, 35). Farther east, in consequence of thinning of the early Pleistocene sediments, Tertiary bedrock also was incorporated into the ice-pushed ridges. Structurally, however, the imbricate nature of the ridges remains the same (Richter, et al., 1950).

Stauchrücken und fluvioglaz ale Ablagerungen in Utrecht und Gelderland

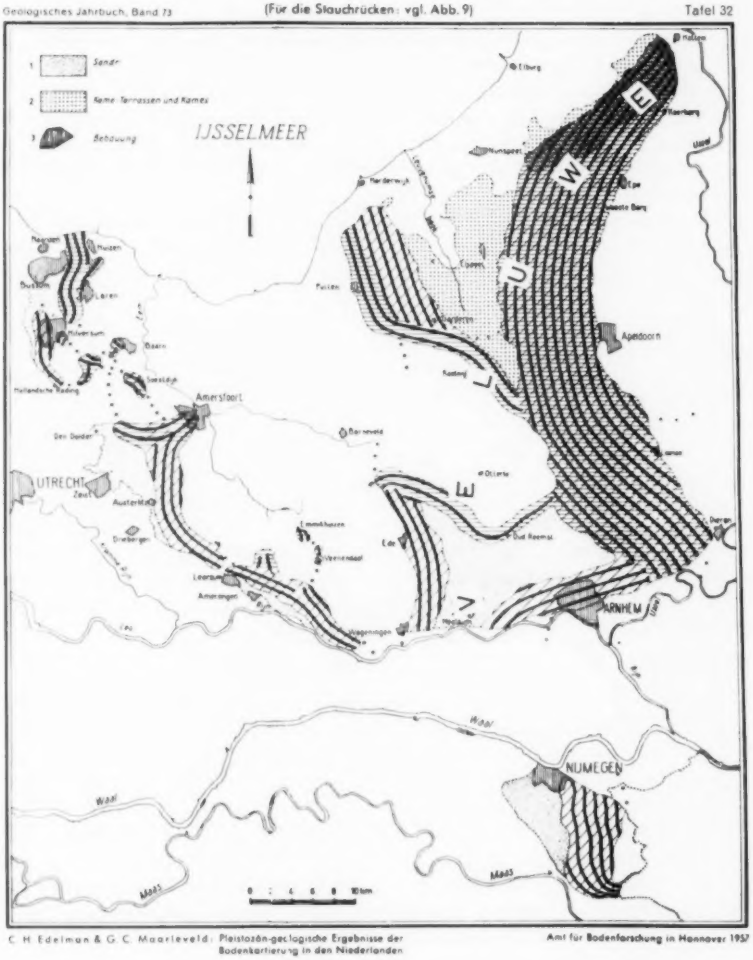

Fig. 2. Structure of the ice-pushed ridges in Central Holland (Edelman and Maarleveld, 1958).

GENESIS OF ICE-PUSHED RIDGES

The genesis of ice-pushed ridges depends on the formation of a thick permafrost soil in front of the advancing ice sheet (Richter, et al., 1950 for western Germany; De Jong, 1952, 1954, for Holland). The permafrost layer formed a hard, brittle sheet. When it broke, whole slices were pushed out of the way, with their original sedimentary structures intact. After postglacial thawing the pushed-up blocks remained largely intact structurally because of the internal friction of the layers of sand, gravel and clay.

The minimum thickness of the permafrost layer thus was equivalent to the thickness of the individual pushed-up blocks within the imbricate cross section of a ridge. As blocks 150 m thick are found, the permafrost layer, on the other hand, probably was not much thicker. It follows that many of the overthrust planes developed at the base of the permafrost layer, where the waterlogged sediments could not offer much resistance to the load and push of the ice sheet.

In areal distribution, ice-pushed ridges show a marked correlation with river valleys. In general, ridges follow the valley on both sides, the structures of the ridges indicating that they have been pushed from the valley axis outwards.

Brouwer (1950) gave an explanation of this correlation with river valleys in Holland. According to him, the advance of the Riss ice sheet was halted for a considerable time in northern Holland, south of Drenthe province. A typical end moraine lies to the north of the area of ice-pushed ridges with till deposits up to 70 m thick. During this stationary period of the ice front, the northward flowing rivers, Meuse, Rhine, Ems, Weser, etc., eroded broad valleys in the northwestern European plain. They were dammed by the ice sheet to the north, and probably had a northwesterly outlet along the ice margin. During a final advance of the Riss ice, individual lobes advanced southwards; penetrating individually into the pre-existing river valleys, and pushing outward the material of the valley walls. By this process, which greatly accentuated the altitudinal differences in the pre-existing valleys, the high ridges were pushed up, while the correlation with the river valleys also becomes clear.

DISCUSSION

Ice-pushed ridges in regional development of such a size and extent seem to be entirely absent in the glaciated areas of the United States. In the plains of northwestern Canada, however, they are present (Slater, 1927; Prof. George White, oral communication). This is of importance for the question of the genesis of these ridges. Also, it is well to note that in Europe ice-pushed ridges of regional extent are also absent in the area of the Würm (= Weichsel; = Wisconsin) glaciation.

The difference between the northwestern European plain where ice-pushed ridges are the main glacial feature, and the American plains where such structures are characteristically absent, can, I think, be explained by the difference in the drainage pattern.

In northwestern Europe the northerly drainage was dammed by the Riss ice sheet (fig. 1). Hence, in front of the advancing ice, there existed a water-

logged area in which a thick permafrost layer could develop. In North America, on the other hand, the southerly drainage tended to keep the area in front of the advancing ice relatively dry. Hence waterlogging of sediments and development of a thick permafrost layer were inhibited. There was no brittle subglacial layer, no sudden break of physical characteristics at the boundary of permafrost and underlying "normal" water saturated sediments. In consequence, none of the factors that favor the development of ice-pushed ridges were present.

This hypothesis is strengthened by the absence of regional development of ice-pushed ridges in the area of the Würm glaciation in Europe, and, conversely, by the presence of such structures in northwest Canada.

In northern Europe, during the Würm glaciation, the drainage was away from the ice sheet, toward the North Sea. The Würm ice sheet did not reach far enough south to dam the north-flowing rivers of the northwestern European plain (fig. 1). Conversely, the drainage pattern in northwestern Canada was from the Rocky Mountains toward the ice sheet. So when and where loose sediments were available, these ought to have become waterlogged. A thick permafrost layer could become established and ice-pushed ridges could develop there.

There seems to be a definite correlation between the direction of the drainage as related to the ice sheet, and the regional development of ice-pushed ridges. This relation may thus well be responsible for the presence or absence of these structures over extensively glaciated plains.

ACKNOWLEDGMENT

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COMMUNICATION

X-RAY MEASUREMENT OF THE IRON-MAGNESIUM RATIO IN BIOTITES

Mr. R. R. Coats of the U. S. Geological Survey has kindly pointed out the omission of credits for some of the analyses of biotites in my paper published in this Journal (1957, v. 255, no. 2, p. 142-156). He suggested publishing a supplementary note giving the necessary credits.

Sample B7 from the M.I.T. collection was described by S. R. Nockolds (1947, Am. Jour. Sci., v. 245, p. 401-420).

Sample B9 was analyzed by J. J. Fahel (*in* Coats, R. R., and Fahey, J. J., 1944, Am. Mineralogist, v. 29, p. 373-377).

Sample B19 was analyzed for me at Cambridge (C. E. Tilley, personal communication).

Sample B23 was obtained from Anna Heitanen of the U. S. Geological Survey and was analyzed by R. N. Eccher (personal communication).

Sample B24 was anaylzed by R. E. Stevens (*in* Hess., F. L., and Stevens, R. E., 1937, Am. Mineralogist, v. 22, p. 1040-1044).

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Vancouver 5, B.C.

REVIEWS

Vector Space and Its Application in Crystal-Structure Analysis; by MARTIN J. BUERGER. P. xiv 347; 186 figs. New York, 1959 (John Wiley and Sons, Inc., $12.00).—The only basic difficulty that stands in the way of the routine solution of crystal structures (aside from questions concerning resolution of atomic details) stems from the fact that while in the diffraction experiment the intensities of the diffracted beams are readily measurable, the necessary relative phases of these beams are not measurable. Three principal methods of attack have been developed in attempts to ovrcome this difficulty. In the two recently developed methods, the method of inequalities of Harker and Kasper, and the statistical methods of Hauptman and Karle, and of other workers, advantage is taken of the symmetries of crystals and the usual redundancy of intensity data to calculate at least some of the phases directly from these intensity data. The third, and now classical method, published by A. L. Patterson in 1934, bypasses the phase problem: Patterson showed that it is possible to calculate the interatomic-vector distribution in a crystal using as experimental data only the intensities. As a result of this discovery the basic problem then became, for the great majority of crystal-structure analyses, the problem of the recovery of the atomic distribution from the vector distribution. The present book is concerned solely with the properties of interatomic vector space and its use in working out crystal structures, and offers for the first time a complete treatment of the subject.

With this volume Professor Buerger has added still another to the growing collection of eminently useful books on various aspects of crystallography that have appeared under his authorship. *Vector Space* is a lucid, detailed, and

comprehensive treatment. As with his previous books, the author has here approached the subject in as elementary a way as is consistent with the demands of the subject matter. The mathematical treatment of the porperties of interatomic vectors is extended and self-contained, and requires no particularly specialized prior knowledge on the part of the reader. For the application of the interatomic-vector function, i.e. the Patterson function, to the solution of crystal structures some general knowledge of crystallography is presumed. In particular, it is necessary to have a working knowledge of the symmetry properties of crystals.

Approximately the first two-thirds of the book is devoted to an exposition of the theory of the Patterson function in its original and modified forms, the use of symmetry considerations in vector space, and to many examples of structures solved by the Patterson method. Among the topics treated are special kinds of Patterson functions, such as generalized Patterson projections and weighted Patterson projections, the theory of homometric sets and structures, Harker sections, and the implication and symmetry-in-vector-space developments due to the author. In the third portion of the book attention is turned to the theory and methods for recovering the electron-density function from the Patterson function in two or three dimensions. This is a recent development of immense practical importance, and one to which the author himself has made many important contributions. This section contains many illustrative examples of original crystal-structure determinations carried out by the author and his students.

The entire book is characterized by many excellent drawings, detailed tables, extensive bibliographies, and a comprehensive index. A very welcome feature of the book is the detailing of practical procedures for carrying out some of the operations involved in a crystal-structure determination. The physical properties of the book are excellent in every respect.

This book can be recommended without qualification. It will be equally useful as a textbook for the student and as a working reference volume on the desk (or drafting-table) of the more experienced crystallographer. Professor Buerger is to be congratulated on his achievement, and to be thanked for sharing with us his comprehensive knowledge and broad experience in this field.

C. L. CHRIST

Dendritic Crystallization; by D. D. Saratovkin (translated from the second Russian edition by J. E. S. Bradley). P. 126; 88 figs. New York, 1959 (Consultants Bureau, Inc., $6.00).—This interesting and largely descriptive book is "directed to metal-working engineers, and may be of use to college students." It contains few ideas that will be new to the research worker in metallurgy or crystallography, but the novelty and quality of the presentation will make it a useful evening's reading even for these advanced workers; it should be a useful outline of important ideas for intensive reading by the student or practical engineer, though such persons should be warned to keep in mind the limited field of interest stated in the title.

The book reviews the state of prior knowledge in some detail from the Russian point of view (Russian references in the bibliography outnumber

foreign ones 103 to 24). The emphasis is strongly slanted toward the work of the Russian crystallographers and metallurgists, particularly D. K. Chernov whose works appeared between 1860 and 1885. The author's views and theories about dendritic crystal growth are supported by excellent photomicrographs, many of them stereoscopic and usable without special lenses, prisms, or viewers. There is no attempt to separate clearly or explicitly the author's contributions to theory from those of previous workers. Dendritic, feathered, and skeletal crystals are distinguished and figured; "antiskeletal," or spiral-growth patterns are noted briefly; some good experimental work with ammonium chloride and other salts is described and beautifully illustrated; eutectic solutions and melts, and the related contact-fusion phenomena are described; and a brief section relates these concepts to practical problems of the steel foundry. In the final section, Chernov's work is again praised, and the conclusion is emphasized that the new experimental data are compatible with the old hypothesis that dendritic crystal growth must be due to impurities "which always occur." Although such impurities should be detectable by modern techniques, they do not seem to have been sought for explicitly. This work should interest many readers; it is recommended mainly for the careful descriptive detail of the experimental work.

An appreciation is due the translator for his work in rendering this book into clear, readable English. For some purposes it would be better to include the original Russian title-page, and perhaps also original spellings in Cyrillic alphabet for authors and titles of works cited in the bibliography.

HORACE WINCHELL

Lower Tertiary Biostratigraphy of the California Coast Ranges; by V. Standish Mallory. P. viii + 416; 7 figs., 42 plates, 19 tables, Tulsa, 1959 (American Association of Petroleum Geologists, $12.00).—This comprehensive review provides data on the occurrence and stratigraphic distribution of foraminifera in the Paleocene and Eocene deposits of California, with illustrations of many forms and descriptions of a number of new species. It also seeks to set up a series of provincial stages and foraminiferal zones for the pre-Oligocene rocks of California, to complete the system established in the later Tertiary by R. M. Kleinpell, H. G. Schenck, and others. It thus may be regarded as a companion volume to Kleinpell's "Miocene Stratigraphy of California", a work which is again available in reprint form.

The author proposes a "standard" chronologic-biostratigraphic section for the lower Tertiary of California on the basis of complementary sections in Kern County, which approach as closely as possible the ideal of an uninterrupted fossiliferous sequence with demonstrable superposition and adequate paleontologic control at both top and bottom. Ten zones characterized by distinctive formaminiferal assemblages are defined, and grouped into five "stages".

Unlike the later Tertiary stages used by micropaleontologists in the Pacific Coast Province, which differ appreciably in scope and limits from the time-stratigraphic units used by students of larger invertebrates, these stages proposed by Mallory appear to correspond almost exactly with the generally

used "megafossil" stages of the Paleocene and Eocene. Although he points out difficulties of correlation with these units, owing to the general absence of foraminifera in the near-shore sandstones in which molluscan faunas occur, and vice versa, no definite example of non-parallel application of the two terminologies can be found in the book. The foraminiferal zones are extremely useful for subdividing shale sections; frequently several zones occur within a thin shale unit, as in the Lodo formation on Media Agua Creek. But the value of the new stage terms is not apparent, and the introduction of a parallel set of names to those used by other paleontologists and stratigraphers can only serve to make an already exceedingly complex terminology still more confusing.

Unfortunately Mr. Mallory's attempt to set up a rigid standard section has its shortcomings. No type localities are mentioned for the two zones of the Penutian Stage, and only by inference are the types of the succeeding two zones of the Ulatisian in the Vacaville Shales of Solano County; the remainder are defined on the basis of the "standard" sections. For reasons which are unclear to this reviewer, the "stages" are defined, not on the basis of the "standard" sections but from a variety of localities. The Ynezian and Bulitian are based upon parts of the Anita Shale of Arroyo el Bulito near Santa Barbara, where the same zones recognized in the "standard" section are well developed. The Penutian Stage is stated to have its locality on Media Agua Creek in Kern Co., but "the type includes the 20 feet of olive to greenish gray siltstone and shale whose lower portion constituted the type of the Bulitian Stage . . . " (p. 34) which was stated on p. 30 to be "120 feet of olive green mudstone and siltstone of the Anita formation" in Arroyo el Bulito. The Ulatisian stage is described from Solano County, and only the highest stage, the Narizian, is established on rocks of the "standard" section.

Careless omission of words, indefinite antecedants, and barbarisms such as "unmegafossiliferous" tend to distract the reader and obscure the author's ideas. This is regrettable, for the basic content of the volume, its range charts, systematic list, and illustrations, form a valuable tool for stratigraphers and students of foraminifera.

JOSEPH T. GREGORY

Basic Data of Plasma Physics; by SANFORD C. BROWN. P. vii + 336; 339 figs. New York, 1959 (John Wiley & Sons, Inc., $6.50).—Before the Second World War the subject of gas discharges was in the doldrums, uninteresting, out of the way of spectacular physical researches and noticed only by a few devotees. The practical exigencies of the war with its development of radar changed the attitudes of physicists, and largely because of the inspired and painstaking work of the author of this book, the field of discharges became rich, fascinating and full of promise for attainment of further fundamental knowledge.

In this small volume Brown has collated the primary data which he and others have gathered. Collison cross sections of various sorts for electrons and ions, coefficients pertaining to ionization, primary and secondary emission of electrons are presented, mostly in graphical or tabular form. Facts having to do with microwave discharges receive special and authoritative attention. The small size of the book and the author's inclination limit the treatment of theo-

retical matters to all but the very simplest versions; particle mechanics rather than kinetic theory and statistical mechanics form the basis of nearly all explanations, distribution functions being rarely introduced. While this feature circumscribes the usefulness of the book for the theorist, it provides a unity of conception as well as pedagogical advantages for the novice which give the book distinction.

HENRY MARGENAU

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